

Ecological Risk Analysis of Elevated Metal Concentrations in the Spokane River, Washington

November 6, 2000

Matt Kadlec, Ph.D.

Prepared for the
The State of Washington Department of Ecology
Toxics Cleanup Program
P.O. Box 47600
Olympia, Washington 98504-7600

Contract C0000233

Table of Contents

Introduction	1
Characteristics of the Toxicants of Concern.....	2
Bioavailability	3
Water Column Contamination Trends	3
Biological Assays Using Algae	6
Biological Assays Using Invertebrates	6
Biological Assays Using Fish	9
Water Quality Criteria and Benchmarks	9
Sediment Exposure Effects Assessment	11
Sublethal Effects	18
Toxicity of Mixtures	19
Bioaccumulation and Biomagnification.....	20
Phytoplankton	20
Macroinvertebrates	20
Fish Tissues	24
Interactive Effects.....	30
Acclimation to Metal Stress	31
Primary Productivity Assessment.....	31
Macroinvertebrate Community Assessment.....	33
Taxa Richness	34
Ephemeroptera, Plecoptera, Trichoptera, and Chironomidae Abundance	35
Percent Contribution of Dominant Family	37
Fish Community Assessment.....	38
Piscivorous Bird Assessment.....	47
Population Fitness.....	48
Data Summary	49
Water Column Risk Summary	49
Sediment Risk Summary	50
Risk Characterization	52
Primary Productivity	52
Macroinvertebrate Community	52
Fish Community	54
Piscivorous Birds.....	56
Conclusions.....	57
References.....	60

Tables

Table 1. Summary of Spokane River dissolved metal levels, July 28, 1992 – Sept. 8, 1993	5
Table 2. As, Cd, Pb, and Zn invertebrate toxicity data from U.S.EPA Water Quality Criteria.....	7
Table 3. Ecological benchmarks for water biota.....	10
Table 4. Ecological benchmarks for sediment biota	12
Table 5. Trace elements in Spokane River sediments of < 2-mm particle size.....	13
Table 6. Trace elements in Spokane River sediments	17
Table 7. Trace elements in Caddisfly tissue from sites on the Spokane River, July 1999	21
Table 8. Mean metal concentrations in CdA, Spokane, and Clark Fork Rivers Caddisfly composite tissues.....	22
Table 9. Average Rainbow trout skeletal muscle tissue metal concentrations – 1998 sample at Seven Mile	26
Table 10. Average metal concentrations in Largescale sucker livers from the Spokane River, 1998-1999	28
Table 11. Organochlorine compounds in whole Largescale suckers and Rainbow trout skeletal muscle, Spokane River, 1998-1999.....	29
Table 12. Riffle-dwelling macroinvertebrate taxa, Spokane River, July 1999	34
Table 13. Spokane River fish taxa, weights, and lengths, 1998 and 1999	43
Table 14. Spokane River fish health indicator data, 1998 and 1999	46
Table 15. Comparison of dissolved metal concentrations to Water Quality Criteria and other ecological benchmarks	50
Table 16. Sediment risk summary and river reach scores.....	51

Figures

Figure 1. Seasonal patterns of total recoverable lead and zinc in the Spokane River, Dec. 1998 - Sept. 1999	4
Figure 2. Results of bioassays on sediments from the Spokane River.....	8
Figure 3. Sediment metals concentrations and ecological effect benchmarks, Spokane River, 1998.....	14
Figure 4. Sediment Pb and Zn concentrations, Spokane River, 1999	16
Figure 5. Caddisfly trace element data, Spokane River, 1999	21
Figure 6. Metals in Whole fish and Crayfish, Spokane River, July 1999.....	23
Figure 7. Relative Zn accumulation by different tissues in fishes of the Spokane River	25
Figure 8. Largescale sucker liver metals from sites on the Spokane River, July 1999.	27
Figure 9. Primary production measures - Pheophytin a, and Chlorophyll a, Spokane River, 1999.....	32
Figure 10. Ash-free dry mass of periphyton per unit surface area of riffle substrate, Spokane River, 1999.....	32
Figure 11. Number of Taxa, Spokane River, 1999.....	35
Figure 12. Ephemoptera, Trichoptera, and Chironomidae abundance in the Spokane River, 1999.....	36
Figure 13. Contribution of dominant family to total abundance in the Spokane River, 1999.....	37
Figure 14. Fish community, Spokane River, 1998 and 1999.....	40
Figure 15. Fish health indicator data, Spokane River, 1998 and 1999	46

Abstract

This report summarizes Spokane River water, sediment, and biological data; reviews scientific literature relevant to the impairment of resident species; and presents a synthesis of available information in order to quantify the extent and magnitude of ecological effects from contamination of the river by metals. Zinc is the primary stress-inducing agent. The ecological effects of this and other enriched elements are discussed. The aggregate effects of multiple metals, other man-made contaminants, and excessive water temperature are considered in overall risk. There is substantial evidence of metal induced ecological degradation in the Spokane River progressively increasing in severity upstream, nearer the metal sources in Idaho. However, the river may be on the threshold of some ecological recovery, provided the decline in water-column metals concentrations that was evident in the 1970s resumes. In more recent decades the river has not enjoyed similar declines in metals concentrations. In addition to improvement in water column metals levels, contaminated sediments would need to be remediated, other stressors would also need to be reduced, and habitat conditions improved in order for continued ecological recovery of the Spokane River. Evidence is provided along with associated uncertainty supporting conclusion of impacts, which range from minor to severe in various components of the ecosystem.

Acknowledgement

I would like to thank John Roland and Art Johnson for their input and careful reviews of this report.

Introduction

The Spokane River (SR) flows out of Coeur d'Alene (CdA) Lake from Idaho into Washington. The State of Washington Department of Ecology (WDOE) has documented elevated levels of the metals cadmium (Cd), lead (Pb), and zinc (Zn) entering Washington via the river. These elements are derived from historic mining and ore-processing areas within the CdA Basin in Idaho. Tailings discharged into the CdA River have been transported and deposited along the river channel and flood plain into CdA Lake and out of the lake into the SR. Spring runoff and occasional floods redistribute and transport trace element-enriched sediments through the SR, downstream to the Columbia River (Bortleson et al., 1994). Various studies have found elevated levels of these metals in surface water, sediment, macroinvertebrates, and fish in the SR, including free flowing reaches and in its largest impoundments: Long Lake, and Lake Roosevelt. Data on the SR were obtained from sources including USEPA STORET System (1970-1997), WDOE Ambient Monitoring Data (1970-1996), and other studies. This report reviews and interprets recent and historic SR data with relevance to the ecological condition of the river.

Extensive effort is under way in the SR Basin to evaluate and then mitigate the adverse environmental effects of past mining and ore-processing activities. Much of this effort is focused within the South Fork CdA River where, in 1983, EPA established the Bunker Hill Superfund Site, under the authority of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA). This site is a 5-km² area that encompasses the Bunker Hill complex in Kellogg, ID. Site-specific activities such as sediment removal, reclamation, and stream-channel rehabilitation are being conducted in the South Fork CdA River by the State of Idaho, various Federal agencies, and mining companies. In the early 1990's, Federal agencies and the CdA Tribe began the CdA Basin Natural Resources Damage Assessment, which encompassed the entire CdA Basin (Raucher et al. 1990; Ridolfi Engineers. 1995; and others).

More recently, the State of Idaho came under court order to develop a Clean Water Act-mandated total maximum daily load (TMDL) for Idaho waters within the SR Basin. The TMDL addresses the allocation of loads of trace elements as well as nutrients and sediment (USGS 1997). In addition, the Washington State Department of Ecology Water Quality Status Report has placed the SR on its 303(d) list (WDOE 1996). Cd, Pb, and Zn from the CdA Basin in Idaho the major reason for violation of Washington's water quality criteria. The SR is considered likely to sustain excessive background loading for many years (Pelletier, 1994).

The EPA recently initiated a Remedial Investigation/Feasibility Study (RI/FS) of the SR Basin under the authority of CERCLA, which requires EPA to evaluate contaminant release, fate, and transport. The RI phase involves data collection to characterize site conditions, develop conceptual models, determine the nature and extent of trace-element contamination, and conduct risk assessments for human health and the environment. It also includes a basin-wide ecological risk assessment. The development and evaluation of remedial action alternatives is the focus of the FS. Much of the RI/FS effort has been focused on the upper CdA Basin. Review of the available data on the Spokane River presented in this report, suggests greater attention is needed to address the serious impacts in this portion of the watershed.

Characteristics of the Toxicants of Concern

Zn is an essential element - acting as a cofactor of many enzyme systems - in all organisms; however, because its window of essentiality is relatively small, it can be toxic to aquatic organisms at high concentrations. The concentrations of Zn in SR media (surface water and sediment), particularly segments of the river nearest to Idaho (Soltero 1977; USGS and WDOE, unpublished), are well above normal background levels, and beyond the window of essentiality. The metalloid arsenic (As) may be essential in extremely minute quantities but its physiological role is speculative. The concentrations of As are above any window of essentiality, and appear slightly elevated in sediment in places. WDOE's ambient water quality monitoring show 0.33 – 0.5 ug/L total recoverable As at the State line (monitoring using appropriate detection levels was limited to 1996 – 1997) (Johnson, personal communication). Recent USGS data have shown background levels of 10 ppm in sediments in other parts of the region, yet the U.S.EPA Human Health Screening Assessment of the Spokane River has reported As in the 13-19ppm range (Roland, personal communication). Cd and Pb have no known physiological role in normal biological processes: toxic effects are thought to accompany any tissue accumulation. Cd and Pb concentrations in the Spokane are above background levels.

Arsenic inhibits respiration. It can exist in water in several forms, but the most stable form is arsenate (H_2AsO_4^-). Arsenate is transformed in vivo to arsenite, which induces oxidative damage. Arsenate can be bioaccumulated following phosphate pathways. The negative effects of Cd on survival, growth and reproduction can often be detected at about a tenth of the concentration (by weight) at which they occur with Zn. Consequently, if the concentration of Zn is ten times that of Cd then toxicity will be due to both metals equally. However, in SR water, Zn is usually present at about 60 times the concentration of Cd. Thus, Zn is primarily responsible for toxic effects via water exposure.

A wide range of effects of Pb occur in plants. Pb has been shown to interfere with cell wall formation, synthesis of structural proteins, absorption and transpiration, seed viability and germination. Pb causes reduction of photosynthesis, adenosine triphosphate formation, and growth. In animals, Pb is a nonspecific toxicant acting to inhibit many of the enzymes necessary for normal biological functioning. The most studied effects are on the hematological system, the brain and nervous system, learning and behavior, and reproduction and survival.

Metals may act at many cellular sites to produce a variety of toxic effects. For example, calcium receptors at the gill are vulnerable to competition by certain metals, which can upset normal function. Some metals inhibit Na/K-ATPase. Na/K-ATPase is an energy requiring enzyme that maintains normal cellular membrane potential by acting as a sodium-potassium pump. Inhibition of Na/K-ATPase may in turn upset ionoregulatory balance (Reid and McDonald, 1988). Fish and other aquatic organisms continually gain ions during normal development (Shearer 1984; Lauren and McDonald, 1985) and upsets may affect survival and growth (Frag et al. 1993).

Lipid peroxidation is another consequence of metal uptake. Cellular lipid membranes are damaged by metal-induced peroxidation. Metals existing in more than one valence state act as catalysts for lipid peroxidation (Wills 1985). Lipid peroxidation can compromise the balance of fluidity and structure by damaging polyunsaturated fatty acids located in cellular membranes. This damage can decrease fluidity, increase leakiness, and inactivate membrane-bound enzymes, changes that ultimately result in tissue damage and cell death (Halliwell and Gutteridge 1985; Wills 1985).

Bioavailability

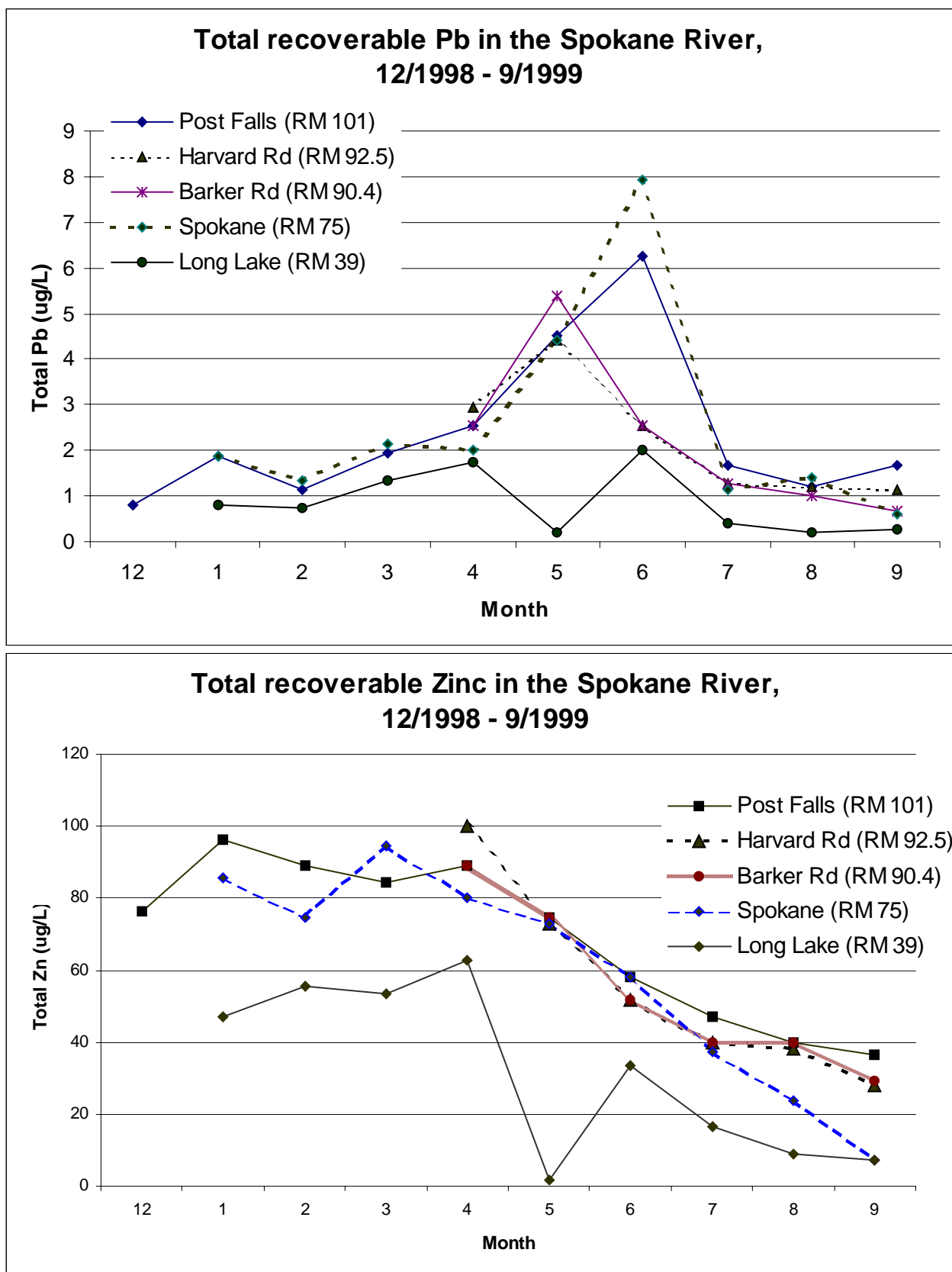
In environmental contaminant studies, consideration must be given to the question of bioavailability. Metals may be present and measurable in environmental media but, at least partially existing in forms that are not available for uptake into organisms. For example, Zn bound to clay particles exerts no measurable toxicity to Rainbow trout; however, most (60-95%) of the Zn in the SR is in the soluble form (Bailey and Saltes, 1982). In Lake Roosevelt, 73% of the Zn was in the <0.45-um (dissolved) phase (Johnson et al. 1990). Pelletier (1994) found average dissolved to total fractions to be 69% Cd; 18% Pb and 83% Zn. In addition, other materials, such as naturally occurring organic and inorganic solids, did not noticeably effect the bioavailability of these metals. The LC50 is median lethal concentration of a material in water that is estimated to be lethal to 50% of the tested organisms after a defined exposure period. When determining Cd, Pb, and Zn LC50s with Rainbow trout, Bailey and Saltes (1982) found no significant effect of the solids in either SR or Columbia River waters on the level of metal toxicities. Thus, while Pb in the river water is mostly on suspended particles, it is still a risk to aquatic organisms.

Water Column Contamination Trends

There is substantial data on metals in the SR water column including but not limited to: USEPA STORET System (1970-1997) [Cd, Pb, Zn]; WDOE Ambient Monitoring Data (1970-1996) [Cd, Pb, Zn]; Stude (1971) (data from USEPA STORET) [Zn, Pb]; Miller (1973) [Zn]; Soltero et al. (1973) [Zn]; Yake (1977) [Cd, Pb, Zn]; Yake (1979) [Zn]; Soltero et al. (1981) [Zn]; Bailey and Singleton (1984) [Zn]; Hoyle-Dodson (1992) [Zn]; Johnson et al. (1994) [Cd, Pb, Zn]; WDOE (1996) [Cd, Pb, Zn]; WDOE (1997) [Cd, Pb, Zn]. While metals concentrations remain elevated and of ecological concern, a review of the history presented by these studies leads to the conclusion that Cd, Pb, and Zn concentrations in river water have decreased since the early 1970s. The 1970s decline is coincident with Federal mandates, which caused mine operations to eliminate tailings discharges from surface waters. Studies also show that concentrations of trace metals in the river generally decrease proceeding downstream from the state line, and that metals concentrations typically increase in proportion to river flow.

A long-term decline in metals concentrations in the river is illustrated by several studies. In overlapping studies by Funk et al. (1983) and Gibbons, et al. (1984), total Zn ranged from 5-225 ug/L at 10 stations from the state line, at River Mile (RM) 98.7, to below the City of Spokane, over the 1979-81 period. The annual weighted mean Zn concentration was ~100 ug/L. More recently, during the unusually high flows that occurred in the SR during April - June 1997, dissolved Zn and Pb consistently exceeded EPA 1995 water quality criteria by factors of 2 to 6, from above the state line (RM 98.7) to Riverside State Park (RM 66.2). Pb and Zn water quality criteria were also exceeded in a sample collected below Long Lake (RM 33.3). The levels of dissolved Pb were 1.38 - 2.69 µg/L. Dissolved Cd and Zn levels (0.120 - 0.440 ug/L and 42.0 - 119 ug/L, respectively) were similar to what had been found from previous sampling during the high flow season (Hopkins and Johnson, 1997). Pb and Zn concentrations in samples taken in 1998 and 1999 exceeded water quality criteria. In addition, Total recoverable Pb and Zn levels during this period are shown in Figure 1 (Roland, unpublished), which is based on USGS water quality data. No data on As or Cd were available. Yake (1979) also detected a long-term improvement in water quality in the SR.

Figure 1. Seasonal patterns of total recoverable lead and zinc in the Spokane River, Dec. 1998 - Sept. 1999



Concentrations of Cd, Pb, and Zn increase with increasing flow in the SR. In 1992 and 1993, Pelletier did a thorough analysis of this phenomenon and found that although metals concentrations were correlated with flow, water quality criteria for dissolved Zn were exceeded at both low and high flows. Criteria for dissolved Cd and Pb were exceeded only at river flows >15,000 cu.ft./sec at the City of Spokane, during March and May, 1993. Concentrations of dissolved Cu were not significantly correlated with flow (Pelletier 1994). Pelletier also found that concentrations of dissolved Cd, Cu, Pb, and Zn typically decrease relative to criteria proceeding from upstream to downstream stations. Pelletier attributed this mainly to increases in hardness, which resulted in increases in metals criteria proceeding downstream, and to decreases in metals concentrations from dilution with groundwater inflows. Concentrations relative to criteria also varied seasonally, with highest values typically associated with highest river flows during winter and spring. Dissolved Cd exceeded standards at RM 96, during the high flow season. Variability of dissolved Cd at RM 96 also suggested a greater than expected risk of concentrations exceeding standards during the low flow season. Pelletier also noted that dissolved Pb exceeded standards at RMs 64.5, 85.3, and 96, during the high flow season. Variability of dissolved Pb at RM 96 also suggests that concentrations can exceed standards during the low flow season because the probable distribution of the observed range of concentrations overlaps federal water quality criteria. Dissolved Zn exceeded standards at RMs 64.5, 85.3, and 96 during the high flow and low flow seasons. Table 1 is a summary of SR data from July 28, 1992 – Sept. 8, 1993.

Table 1. Summary of Spokane River dissolved metal levels, July 28, 1992 – Sept. 8, 1993

River Mile	Dissolved metal (ug/L)			
		Cd	Pb	Zn
96	Max	0.346	0.724	139
	Mean	0.208	0.291	81.8
85.3	Max	0.271	0.788	163
	Mean	0.166	0.243	88.9
64	Max	0.251	0.788	94.3
	Mean	0.128	0.284	59.4

Source: Pelletier 1994

Data from recent sampling by the USGS and analysis of total Zn and Pb in the SR (Dec. 1998 through Sept. 1999) are presented Figure 1 (Roland unpublished). Repeated sampling was conducted at Post Falls, Harvard Road Barker Road, Spokane, and Long Lake (RM 100 ~ 33) by the USGS for the USEPA. These data suggest that dissolved and total Pb and Zn levels may be little if any lower now than in 1992 and 1993, at corresponding river segments. Figure 1 also reveals the seasonal patterns of total Pb and Zn concentrations in samples taken from points between and including Post Falls and Long Lake during 1998 and 1999. Cd data were incomplete; however, the seasonal pattern of Cd is expected to be intermediate to the patterns of Pb and Zn in relation to its aqueous solubility. No analysis of As was performed.

Biological Assays Using Algae

High levels of toxic and potentially toxic metals, determined through monitoring efforts described previously, raised concern for resident aquatic biota. One result of this concern has been the performance of bioassays with SR water using a variety of standard test species to represent the resident biota. Miller et al. (1973) and Funk et al. (1973) used laboratory bioassays with SR water that showed the amount of Zn normally present in the upper SR was inhibitory to the algal test organism *Selenastrum capricornutum*. Algal assays were used by Miller et al. (1973) to define the effects of metals on the potential growth of planktonic algae within the SR. Algal growth potential in the SR from Post Falls, ID, to Riverside State Park, WA, was found to be limited by the high dissolved Zn content (which averaged 112 ug/L). Reduction of Zn, from about 112 ug/L at the City of Spokane Wastewater Treatment Plant (WWTP) to about 20 ug/L at Long Lake Dam (presumably by dilution, sorption, and other mechanisms) enabled algal growth to increase proportionally to the orthophosphate content of the water. Miller et al. (1973) suggested that a 20-fold increase in orthophosphate loading to the SR system upstream from Riverside State Park would have little effect upon the growth of planktonic algae unless the Zn, Cd (and perhaps other metals) content of these waters was reduced. This must not be taken to mean that too much Zn is good because it suppresses eutrophication. It is not, because it causes reductions of sensitive species, allowing population increases of tolerant species: an imbalance with potentially serious ecological consequences.

Evidence supporting the assumption that metals were causing algal growth inhibition was provided by Cummins et al. (1981) who assessed the nutrients in the SR from Lake CdA to Post Falls, ID, by performing freshwater algal assays. The algal yields achieved in the enriched samples were less than the predicted yields, indicating that other limiting nutrients or elevated concentrations of Cd, Zn, and perhaps other metals, were inhibiting algal growth. Evidence supporting the presence of metal toxicity during these assays was the large increase in algal yields in the presence of sodium EDTA, which chelates divalent metals (Cummins et al., 1981), making them unavailable.

Biological Assays Using Invertebrates

Not many species of invertebrates are likely to be quickly killed by the metals concentrations currently observed in the SR. However, there are some species that are likely to be adversely affected (in ways that affect survival or reproduction) by levels of Zn that occur occasionally. Levels of Cd that occur less often may also adversely affect some invertebrate species. The ranges of metal concentrations that are lethal to half the tested individuals of various species of invertebrates in a 96-h exposure (96-h LC50) are listed in Table 2. Ecologically relevant benchmark concentrations are discussed in the section on Water Quality Criteria and Benchmarks, below.

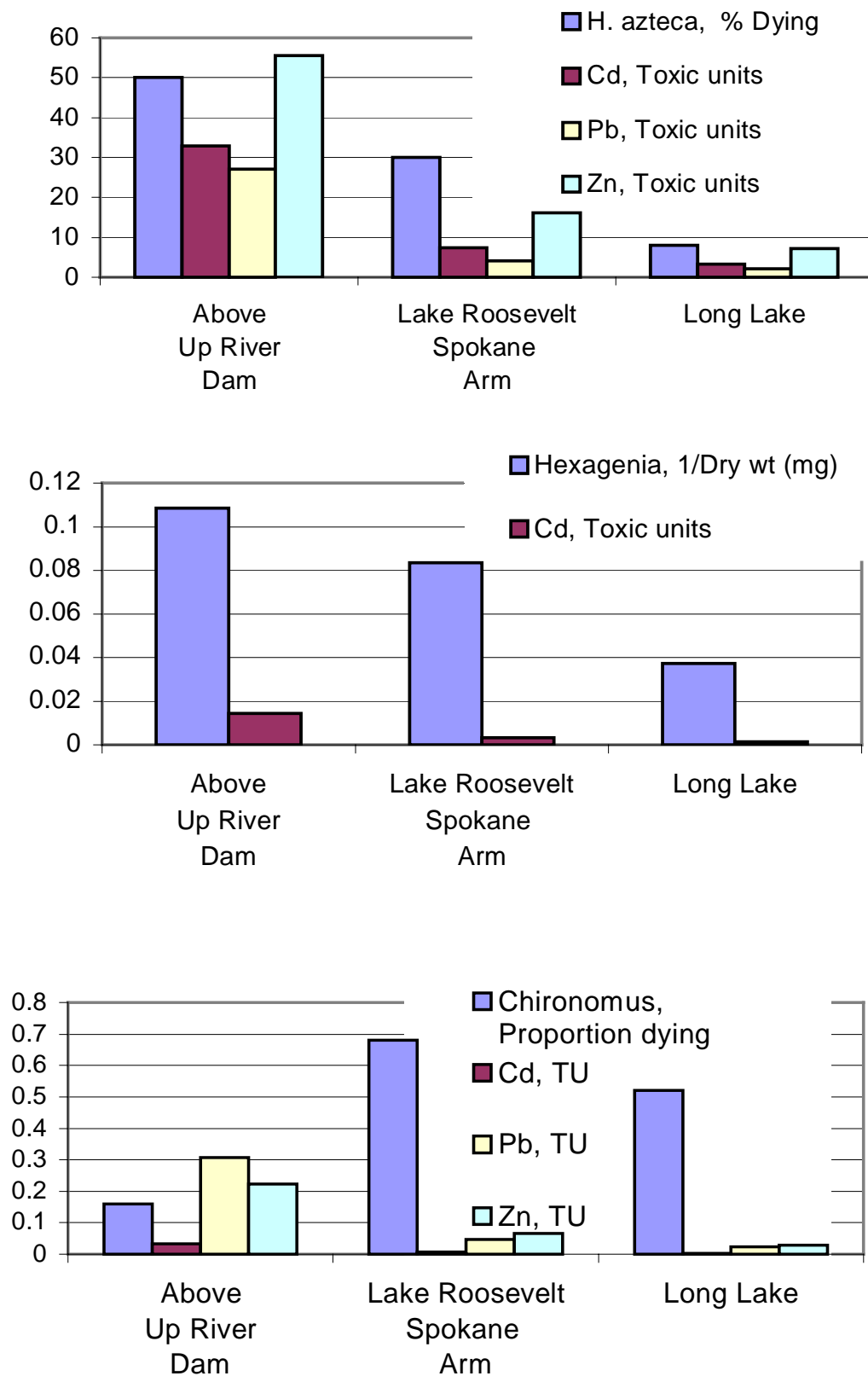
Table 2. As, Cd, Pb, and Zn invertebrate toxicity data from U.S.EPA Water Quality Criteria

96-h LC50 (ug/L)		
Element	Avg. of all	Range
	invertebrates	
As	7690	182 - 22,040
Cd	3091	8.6 - 28,000
Pb	7745	124 - 40,800
Zn	8772	100 - 58,100

Note: Only studies of metallic salts with the same oxidation state are shown.

The Zn concentration exceeds the lower range of species sensitivities in the water column. The total As, Cd, and Pb concentrations do not approach the immediately lethal levels noted in table 2; however, these metals may be present at levels that cause sublethal toxic effects, which could affect invertebrate species population levels. Sediment pore water metals concentrations are unknown, and so their degree of overlap with invertebrate species sensitivity ranges is uncertain. Appropriately, some laboratory bioassays of SR sediments have been conducted using sediment-associated organisms. Results of these bioassays are presented in Figure 2. The results suggest that pore water metal concentrations exceed adverse effects levels for the tested species.

Figure 2. Results of bioassays on sediments from the Spokane River



Biological Assays Using Fish

Some fish species are very sensitive to the concentrations of metals in the range of those seen in the SR. For example, the species *Oncorhynchus mykiss* (Rainbow trout) is one of the most sensitive to Cd. In a flow-through test using 50-mm long Rainbow trout, Cd 100-day lowest observed effect (mortality) levels (LOECs) of 1.74, 5.03, and 5.16-ug/L were determined at three hardnesses (47, 221, 410 mg/L CaCO₃), at 14.3°C (Davies et al. 1993). The Lowest Observed Effect Concentration (LOEC) is the lowest concentration of a material that has a statistically significant adverse effect on the tested population compared to control group.

The Rainbow trout population of the SR appears to have developed resistance to high concentrations of Cd, Pb, and Zn. While tolerance is apparent, ongoing stress is still ecologically significant. This phenomenon will be discussed in the section on acclimation to metal stress, in this report. Other river-dwelling species, chronically exposed to high metals concentrations for the past 100 years, have likely been selected for metals tolerance as well.

Water Quality Criteria and Benchmarks

Comparison of these ecological benchmarks to recent SR metals monitoring data indicates a strong possibility for adverse effects on some species, particularly during periods of high flow in the Spring season when bioavailable metal concentrations are the highest, as indicated by Pelletier (1994) and Roland (unpublished).

U.S. EPA National Ambient Water Quality Criteria and other benchmarks for contaminants of concern in the SR are listed in Table 3. The National Ambient Water Quality Chronic Criteria (NAWQCC) for protection of aquatic organisms are derived from at least eight LC50s and three chronic values. The NAWQCC are the Final Acute Values divided by the Final Acute-Chronic Ratio, which is the geometric mean of quotients of at least three LC50/Chronic-Value ratios from tests of different families of aquatic organisms (Stephan et al. 1985). The duration exposure occurring in the SR indicates that using chronic criteria, NAWQCC, is more appropriate than using acute criteria (NAWQAC). The water quality criteria are intended to prevent significant toxic effects in chronic exposures (Suter and Tsao 1996). If National Ambient Water Quality Criteria were not available for a chemical, as in the case of As V, Suter and Tsao (1996) used the Tier II method from EPA (1993) to calculate Secondary acute and chronic values.

The lowest chronic values (LCV) for fish and invertebrates reported in the literature are another set of benchmarks proposed by (Suter and Tsao 1996). If insufficient chronic value data were available (as in the case of As V), they estimated chronic values by extrapolation from 96-hour LC50s.

Another potential lower benchmark is the Test Effective Concentration 20% (Test EC20) for Fish, which Suter and Tsao (1996) defined as the highest tested concentration of a material in water that is estimated to cause less than 20% reduction in (1) the weight of young fish per initial female fish in a full life-cycle or partial life-cycle test; or (2) the weight of young per egg in an early life-stage test. A similar potential lower benchmark proposed by Suter and Tsao (1996) is the Test EC20 for Daphnids, which is the highest tested concentration causing less than 20% reduction in the product of growth, fecundity, and survivorship in a chronic test with a Daphnid species. These benchmarks are intended to be indices of population production. They are equivalent to chronic values in that they are simply a

summary of the results of chronic toxicity tests. In most cases the same test supplied the lowest chronic value and the lowest test EC20 (LT EC20); however, the test EC20s are based on a level of biological effect rather than a level of statistical significance, and they integrate all of the stages of the toxicity test rather than treating each response independently (Suter and Tsao 1996). Suter et al. (1987, 1992) chose 20% as approximately the mean level of effect on individual response parameters observed at the chronic value concentration, and as a minimum detectable difference in population characteristics in the field. Some test EC20s were estimated values, extrapolated from 96-hour LC50 values using equations from Suter (1992). The LT EC20s for fish and daphnids are provided in Table 3.

The benchmarks referred to as sensitive species (SS) test EC20s are the EC20s, adjusted to approximate the fifth percentile of the species sensitivity distribution. An SS test EC20s is calculated in the same way as a NAWQCC except that test EC20s are used in place of chronic values, and salt water species are not included. The Final Acute Value for each of the toxicants was divided by the geometric mean of ratios of LC50s to EC20s (Suter and Tsao 1996).

The last potential benchmark is the Population Effective Concentration 25% (Population EC25), which is an estimate of the continuous concentration that would cause a 25% reduction in the recruit abundance of largemouth bass. The recruit abundance estimates are generated by a matrix model of a reservoir largemouth bass population. The fecundity, hatching success, larval survival, and post-larval survival of the model population are each decremented by a value generated from statistical extrapolation models (Bartell 1990).

Table 3. Ecological benchmarks for water biota

	As III	As V	Cd	Pb	Zn
NAWQAC*	360		1.05	9.92	28.78
NAWQCC*	190		0.31	1.05	26.07
Secondary acute value		66			
Secondary chronic value		3.1			
LCV Fish	2962	892	1.7	18.88	36.41
LCV Daphnids	914.1	~450	0.15	12.26	46.73
LCV Non-Daphnid inverts.				25.46	>5243
LCV Aquatic Plants	2320	48	2	500	30
LCV All organisms	914.1	48	0.15	12.26	30
LT EC20 Fish	2130	1500	1.8	22	47
LT EC20 Daphnids	633	>932	0.75		
Sensitive Sp. Test EC20	55		0.013	0.35	21
Population EC25	1995	185	4.3	71	80

* NAWQAC and NAWQCC for Cd, Pb, and Zn are hardness dependent. Reported values are calculated for dissolved metals at a water hardness of 19.1-mg/L as CaCO₃ (the lowest hardness reported during the 1992-3 period by Pelletier (1994)).

Note: All concentrations reported in ug/L

Sources as cited by Suter, 1996; and Suter and Tsao, 1996.

Sediment Exposure Effects Assessment

The sediments of the SR have long been known to have elevated concentrations of As, Cd, Pb, and Zn relative to normal background levels. The U.S. Bureau of Fisheries conducted a survey of pollution of the CdA River and adjacent waters (Ellis 1940). In that study, Ellis found Pb and Zn along the SR in Washington. He stated "Soil samples from the banks of the SR near Greenacres, Washington contained Pb and Zn, as evidence of mine slimes or their products being carried across Lake CdA and down the SR". Lingering impacts to river sediments have been confirmed by recent studies conducted by the U.S. EPA (2000) and Horowitz (in press). While tailings and slimes are no longer being discharged, localized Cd, Pb, and Zn contamination of sediments remains, especially above the Upriver Dam impoundment.

Other studies confirm that upstream areas in Idaho are the source of these metals. Matuszak et al. (1996) reported that surface sediments in the upper SR are enriched in Cd, Pb, and Zn relative to unaffected sediments. Ikramuddin (1996, 1997) and Ikramuddin et al. (1997) found $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios were similar to those found in the ore of the CdA mining district. USGS studies sponsored by the U.S. EPA, under CERCLA, further confirm that area as the origin of contamination (USGS 2000).

SR sediments, especially those within its impoundments, act as an important sink for surface water trace elements based on the results of the experimental studies of Cd, Pb, and Zn sorption by river sediments. Zheng (1995) speculated that a metal balance, regulated by sorption/dissolution process, exists between sediments and river water in response to the seasonal pH fluctuations. Seitz and Jones (1981) measured changing pH values from 7.3 to 8.8 in June, August, and November. They speculated that when the pH is high, adsorption and co-precipitation of metals onto Mn/Fe coatings on the river sediments probably dominate. During this period, the bottom sediments may serve as a temporary sink for metals. When the pH is low, those metals may be released by dissolving from the coatings, and become available for transport in solution and biological uptake.

Sediment metal levels were compared to screening benchmark criteria, which may not predict risk of effects as well as pore-water-based benchmarks, but are adequate for this assessment. In many studies conducted on sediments from other locations, toxicity does not correlate well to total metal concentration in sediment; therefore, it is to identify the fraction of the total metal in the sediment pore water that is bioavailable (Hassan et al. 1996). The acid-volatile sulfide (AVS) content of freshwater sediments limits the bioavailability and toxicity of Cd, Pb, Zn, and other divalent metals. The apparatus and instrumentation used for determination of AVS and simultaneously extracted metals (SEM) has been described by Brumbaugh et al. (1996). Briefly, a sediment sample is reacted for 1 h in the absence of oxygen with HCl (1 to 3 N). The H_2S generated is trapped in a pH-12, anti-oxidant buffer and measured with a sulfide electrode. The sediment-acid extract is filtered and analyzed for SEM - Cd, Pb, Zn, and other metals - using graphite furnace atomic absorption, or cold vapor AA for SEM mercury. When the metal-to-AVS ratio is <1 , no metal toxicity is observed. At ratios >1 , metals may be bioavailable (Di Toro et al. 1991; Carlson et al. 1991; U.S. EPA 1995; Ankley et al. 1996). SEM/AVS from Clark Fork River sediments have been shown to correlate with bioaccumulation of Zn and copper (Cu) by *Hyalomma azteca* (Ingersoll et al. 1994). No analyses of AVS have been reported in any SR sediment studies. Had AVS data been available, they would have allowed the

bioavailability, and the potential toxicity of the major contaminant metals, to be more precisely estimated. Still, sediment metal levels can be compared to any screening criteria that do not necessarily require knowledge of actual pore water-dissolved metals concentrations. The trade-off is a decrease in the level of certainty in each prediction's accuracy.

Three sediment ecological effects benchmarks were chosen for comparison to the recent SR sediment metal concentration data. These benchmarks are the Upper Effects Threshold (UET), the Threshold Effects Level (TEL), and the Probable Effects Level (PEL). The UET is the lowest Apparent Effects Threshold (AET) from a compilation of endpoints. AETs relate chemical concentrations in sediment to biological indicators of injury (bioassays, reduced infaunal abundance). They are equivalent to the concentration in the highest nontoxic sample, and represent the concentration at which biological effects would always be expected when that species was exposed to that contaminant alone. Conversely effects are known to occur at levels below the AET (UET) (Buchman, 1999). This is understandable since a UET is a point falling within a range of possible effect levels.

MacDonald (1994) used data from Long et al. (1995) to calculate TELs and PELs. TELs and PELs incorporate chemical concentrations in sediments observed or predicted to be associated with no adverse biological effects (no-effects data). Specifically, the TEL is the geometric mean of the 15th percentile in the effects data set and the 50th percentile in the no effects data set. The PEL is the geometric mean of the 50th percentile in the effects data set and the 85th percentile in the no effects data set. Therefore, the TEL represents the upper limit of the range of sediment contaminant concentrations dominated by no-effects data. The PEL represents the lower limit of the range of contaminant concentrations that are usually- or always associated with adverse biological effects (MacDonald 1994). TEL, PEL, and UET values are presented in Table 4.

Table 4. Ecological benchmarks for sediment biota

	TEL	PEL	UET
As	5.9	17	17 ¹
Cd	0.596	3.53	3 ¹
Pb	35	91.3	127 ²
Zn	123.1	315	520 ³

Note: All levels listed are in mg/Kg, dry wt.

Source: Buchman, 1999

¹ Infaunal community impacts

² *Hyalella azteca* growth reduction

³ Microtox (inhibition of *Vibrio fischeri* bioluminescence)

SR whole sediment metals concentrations data, provided by USGS and WDOE, from their joint 1998 sampling and analysis efforts, indicate levels are often above TEL, PEL, and UET benchmarks. Comparison of these benchmarks to sediment concentration data for the August 1998 samples is presented in Table 5. No whole (bulk) sediment As or Cd data were available for study; however, Pb and Zn levels were similar in both fractionated (<2-mm) and bulk sediments (see Figures 3 and 4). Still, the use of bulk sediment guidelines for comparison to fractionated sediment gives a potentially inflated risk estimate. Nonetheless, the metals of concern are enriched mainly in the finer particulate fractions of sediments, and it is the fine sediment material that provides habitat for most benthic

organisms. Therefore, the comparison is valid. The October through December 1999, USGS sediment sample metals concentrations, along with TEL, PEL, and UET benchmarks, are plotted in Figure 3.

Table 5. Trace elements in Spokane River sediments of < 2-mm particle size

		Post Falls (RM 100) Aug 3, 1998	7 Mile (RM 61.4) Aug 5, 1998
	Reporting limit		
Arsenic	0.1	27.3 ^{1,2,3}	7.77 ¹
Cadmium	0.1	24.4 ^{1,2,3}	3.29 ^{1,3}
Lead	1	1620 ^{1,2,3}	47.3 ¹
Zinc	2	3210 ^{1,2,3}	319 ^{1,2}

Note: concentrations are reported in ug/g (dry wt.)

¹ exceeds TEL

² exceeds PEL

³ exceeds UET

Source: USGS, 2000

The October through December 1998, sediment sample metals concentrations are plotted, along with TEL, PEL, and UET benchmarks, in Figure 3.

Figure 3. Sediment metals concentrations and ecological effect benchmarks, Spokane River, 1998

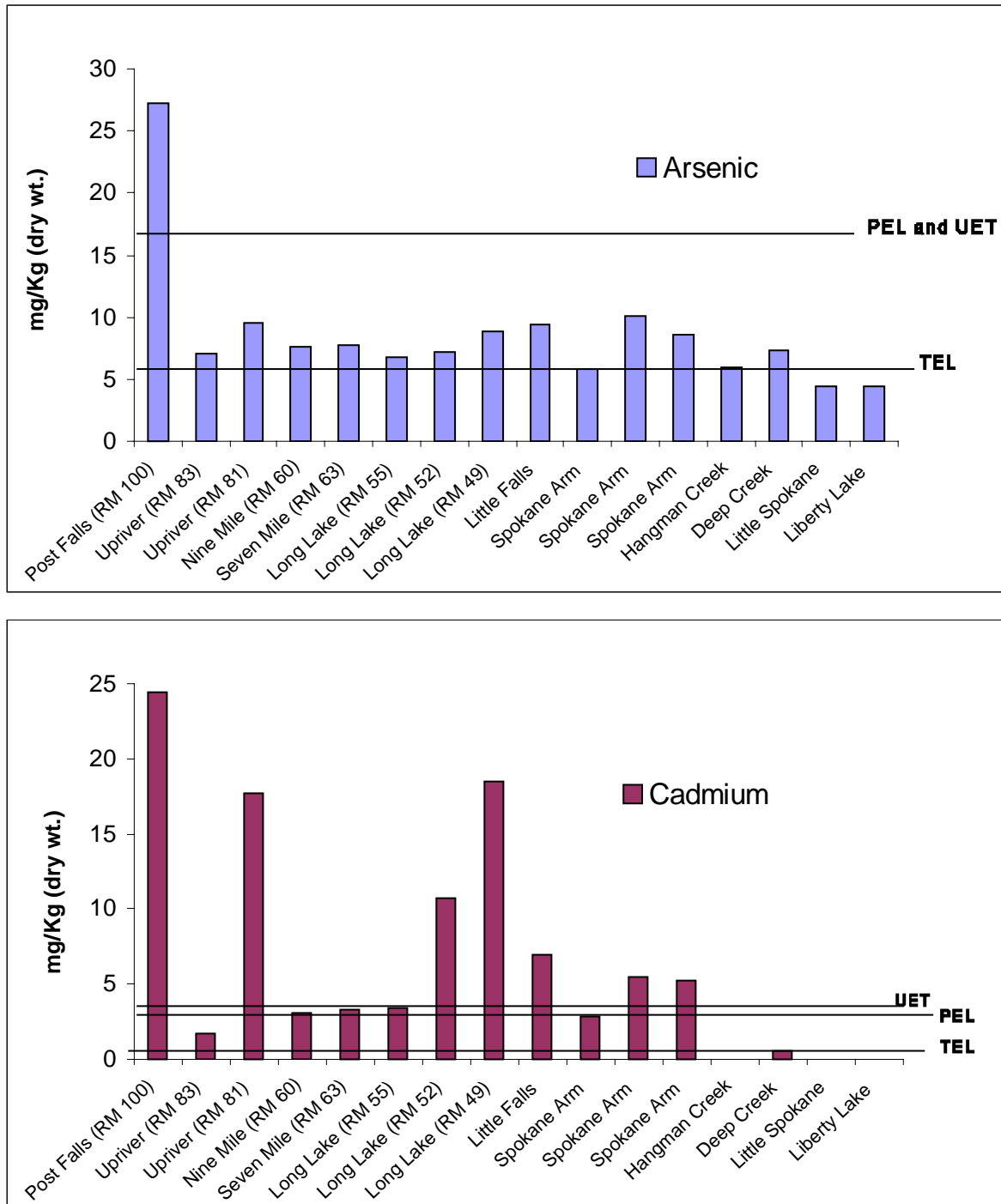
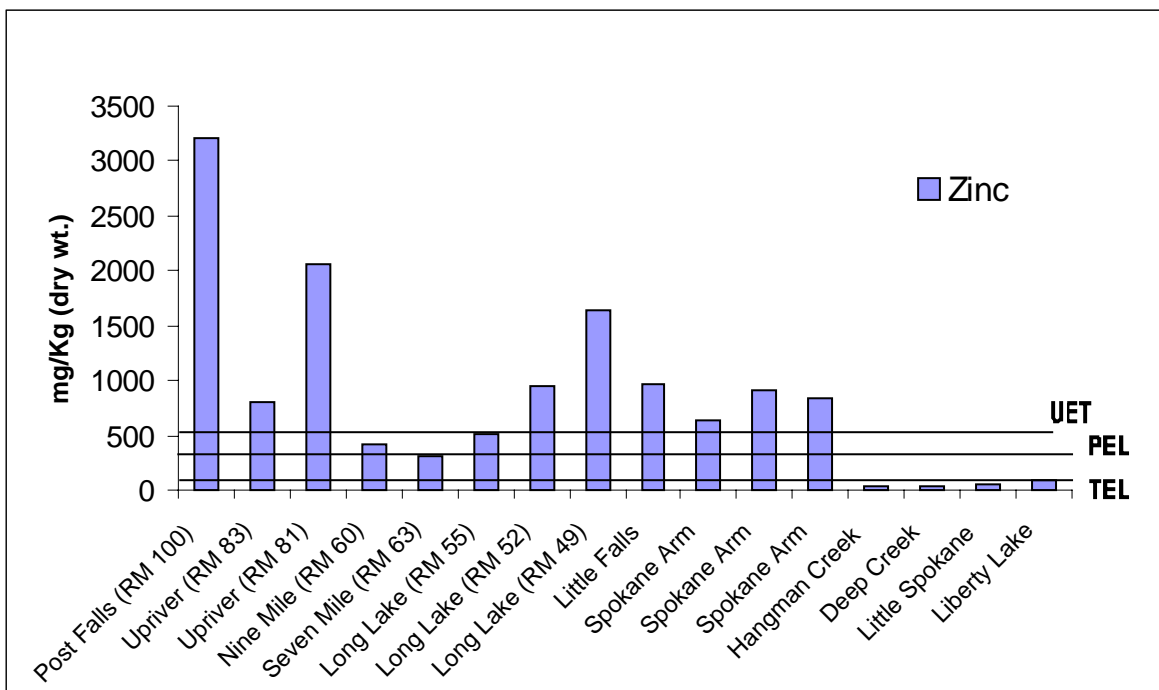
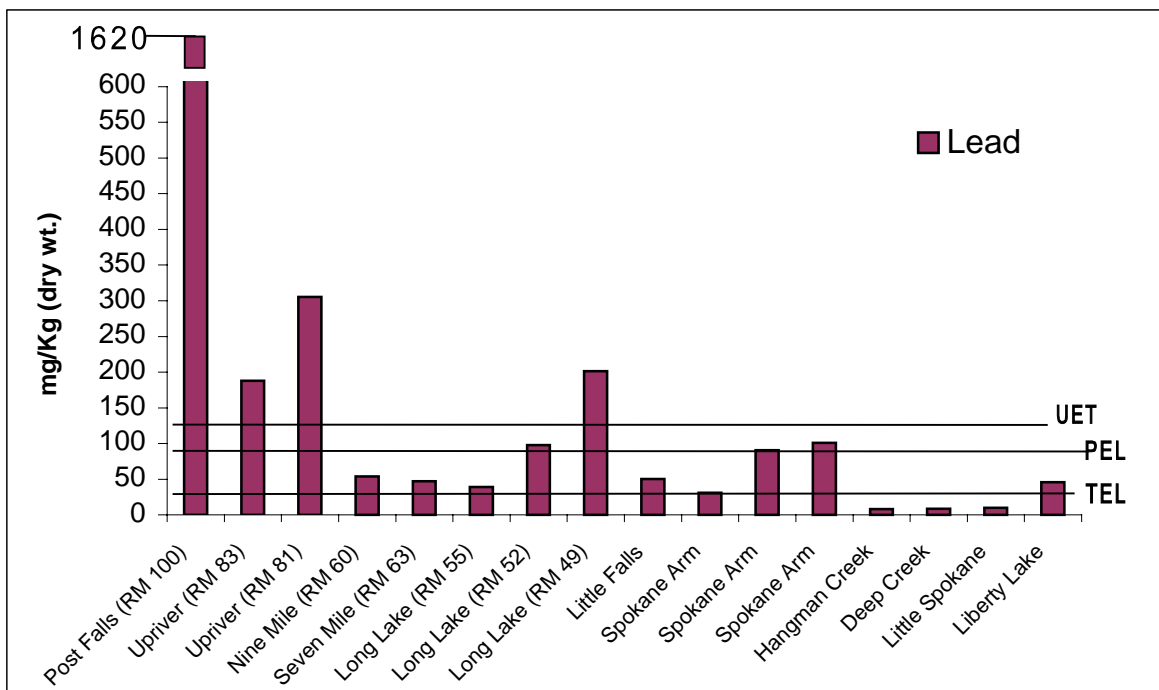
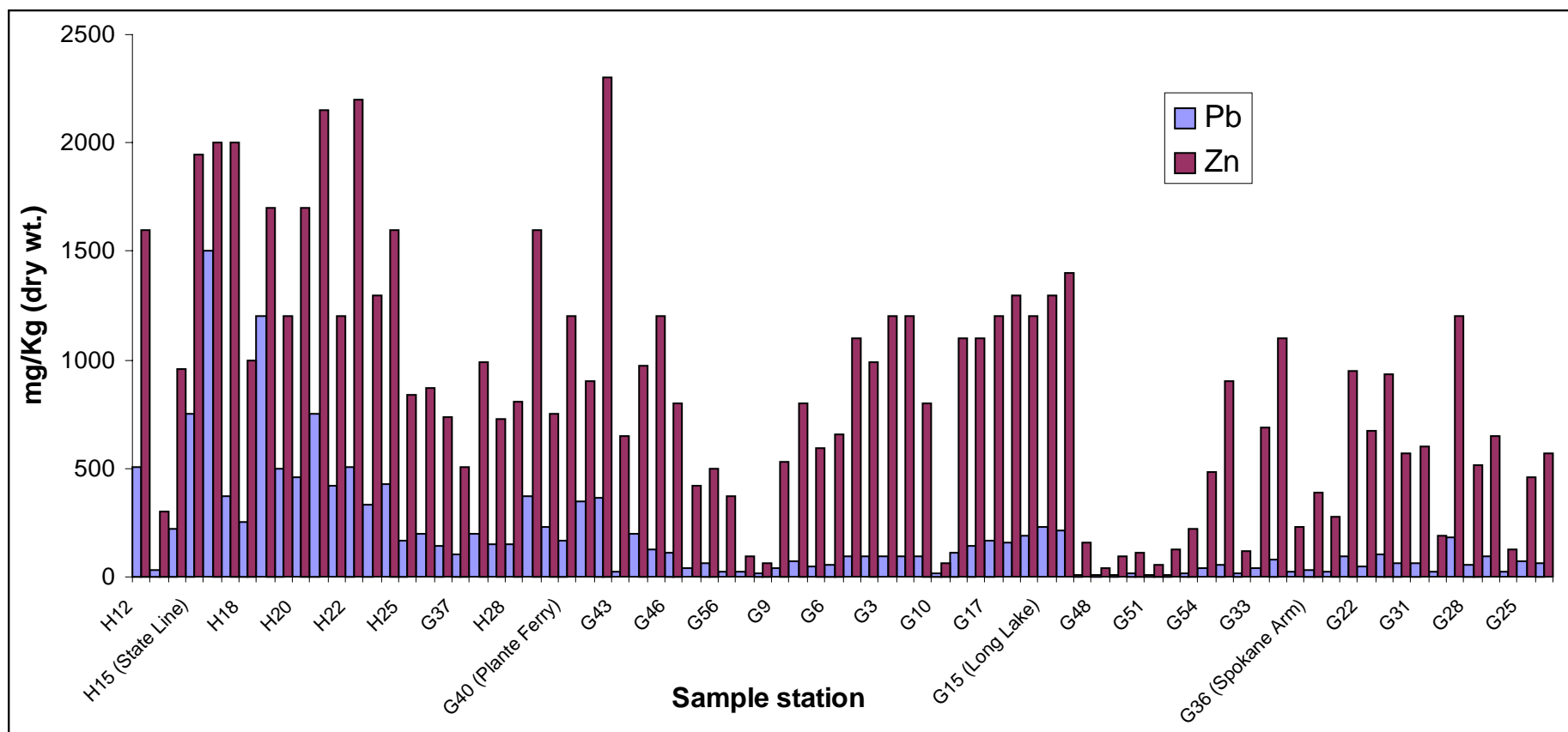


Figure 3. Sediment metals concentrations and ecological effect benchmarks, Spokane River, 1998 (continued)



The USGS reported Pb and Zn (whole sediment, strong acid extraction) analytical results for a series of samples taken along the SR during 1999. These results are plotted in Figure 4. Generally, sediment metal concentrations increase significantly proceeding in the upstream direction.

Figure 4. Sediment Pb and Zn concentrations, Spokane River, 1999



A long-term decline in sediment metals enrichment can be seen by comparing consecutive studies of the past ~30 years. For example, Thomas and Soltero (1977) measured Zn present in sediment cores taken from Long Lake. Zn concentrations in sediments were measured as high as 5,900 ug/g, although concentrations decreased in the upper sediments from the high value, which was measured at a depth of about 200-mm. Johnson et al. (1990) found surface sediments in the Spokane Arm of Lake Roosevelt had 1540 ug/g Zn in 1986. Cd, Pb, and As were also elevated in the Spokane Arm. In 1998, the USGS collected surface sediment samples from the Spokane Arm at 17 locations with the highest Zn concentration being 1200 ug/g.

Violation of benchmark levels indicates the likelihood of sediment toxicity to benthic organisms. This concern prompted Batts and Johnson (1995) to conduct sediment bioassays and metals analyses on samples from three locations on the Spokane River (above Upriver Dam, Long Lake, Spokane Arm). Sediment metals concentrations in the samples they tested are presented in Table 6. The results of the bioassays and measurements are presented in Figure 2 along with Toxic Units (TU) of each metal, for each species.

Table 6. Trace elements in Spokane River sediments

	Above Upriver Dam	Spokane Arm	Long Lake
As	18	29	9.6
Cd	39.6	9	3.91
Pb	542	81	42.3
Zn	4050	1180	520

Note: concentrations are ug/g, dry wt.

Source: Batts and Johnson, 1995

The TU levels provide an explanation for the apparent toxicity of these sediments. TU were calculated from published LC50 data (Rehwoldt et al. 1973; Leonhard et al. 1980; Oladimeji and Offem 1989; Phipps et al. 1995; McLean et al. 1996; Suedel et al. 1997) by equation 1.

$$TU = [metal]/LC50 \quad \text{eq. 1}$$

The purpose of these bar graphs (Figure 2) is to express relative toxicity across sediment stations in terms of metals sensitivities for each of the test species. No LC50 data for As were found for *Hyalella azteca*, *Hexagenia* sp. or *Chironomus* sp., nor was any Pb or Zn data found for *Hexagenia* sp.

While indicating the likelihood of toxicity, the TU calculation is not wholly representative of actual conditions. An influence from pore water AVS is indicated by the apparent reduction of the level of bioavailable metals. *H. azteca* could not be expected to survive a combined >115 TU, as appears to occur in the sample from the Upriver Dam area. It is possible that the AVS in this sediment kept much of the metals that were present in insoluble- non-bioavailable forms. Despite the lack of ideal TU calculations, the relative toxicity of sediments from each site was approximated.

The *H. azteca* and *Hexagenia* sp. graphs (Figure 2) show the clear relationship between metals concentrations expressed as toxic units and test organism response. Batts and Johnson (1995) concluded that *Chironomus* survival results may have been heterogeneous

due to lack of experience with this method among laboratory personnel, or the presence of unknown toxicants, or other factors. In addition to *Chironomus*, *H. azteca*, and *Hexagenia* tests, Batts and Johnson (1995) commissioned a commercial laboratory to perform Microtox tests on SR sediment elutriates and whole sediments. Microtox is a trade name for a test protocol in which the inhibition of *Vibrio fischeri* bioluminescence is measured in response to one or more toxicants. The sediment elutriate Microtox tests revealed a pattern of apparent toxicity corresponding to metals concentration. However, no pattern was observed in the Microtox solid-phase test results, in which *V. fischeri* were exposed to whole sediments. For this reason, these results were not presented in this report. Results using the Microtox Solid-Phase protocol revealed similar heterogeneity to the *Chironomus* tests (Batts and Johnson, 1995).

Assuming high metals concentrations were responsible for the apparent toxicity to different organisms in the Batts and Johnson (1995) study, and that the proportion of bioavailable metals could be nearly the same in any subsequently collected sample, little if any toxicity to these test species might exist for other locations, such as those sampled in 1998 by the USGS, since their reported whole sediment metal concentrations were generally lower than those in the Batts and Johnson (1995) study. Because sediment metals concentrations increase significantly proceeding upstream, there is reasonable probability that sediments are toxic at sites upstream of the upstream-most sample (RM 83) of the USGS-WDOE 1998 sampling effort.

In addition to metals, Polychlorinated Biphenyls (PCBs) have been identified as contaminants of potential ecological concern in the Spokane River. These have originated from past industrial activities along the river. Organic carbon normalized sediment PCB concentrations are highest behind the Upriver Dam (RM 80.6) and near RM 75.4 (WDOE 1995; Golding 1996). Concentrations exceed the Ontario Severe Effects Level), which is a guideline intended to indicate risk to benthic communities (cited by Johnson et al. 1994). Thorough review of PCB contamination and its potential effects on the SR is appropriate but beyond the scope of this report.

Sublethal Effects

Measurement of effects in individuals does not necessarily indicate impacts to entire ecosystems; however, if many individuals are harmed, the well-being of their populations may be at risk. Exposure to metals at elevated (but below immediately lethal) levels can result in adverse health effects in a significant number of individuals. An example of such a non-lethal effect from exposure to some metals is the impairment of physiological ionic balance. For fish in the Clark Fork River, MT, Reid and McDonald (1988) and Farag et al. (1994) found that the ionoregulatory status in adults was not as sensitive to metal exposure as was the ionoregulatory status of juveniles. No significant changes occurred in adult serum ion concentrations. Nonetheless, juvenile fish were affected.

Another sublethal toxic effect of metals is cellular lipid membrane peroxidation. Farag et al. (1994) observed lipid peroxidation in kidneys after 3-weeks of exposure to adult Rainbow trout fed invertebrates collected from the Clark Fork River and held in water with elevated metals. This finding is relevant to the assessment of the SR fish because SR invertebrates are contaminated with higher levels of Cd, Pb, and Zn than invertebrates in the Clark Fork River, as noted in the Bioaccumulation section, below. SR Rainbow trout and other insectivorous fish are exposed to higher concentrations of metals through consumption of contaminated Caddisflies than are Clark Fork River fish. As can be seen in Table 8, among

the Spokane, Clark Fork, and CdA Rivers, Caddisfly tissue metals concentrations are highest in the CdA River. Although comparison of results may be hindered by use of different analytical methods between the studies, there is apparently so much more of these metals in SR Caddisfly tissue than in the Clark Fork River that lipid peroxidation in SR fish is very likely. Unfortunately, no studies exist to confirm or refute this. If this effect is occurring in SR fish, critical organ functions are being impaired, with the result that fish survival may be reduced.

Toxicity of Mixtures

Contaminated freshwater ecosystems often contain a great variety of toxicants that may interact and mutually influence toxicity. However, environmental risk is often judged on the effects of individual compounds without consideration of aggregate effects. Mixture toxicity reflects actual pollution of aquatic ecosystem in a more realistic way than consideration of toxicants singly. Available data on mixture toxicity was reviewed for this assessment; however, very few studies were found that dealt with mixtures resembling those in the SR. Further, no general trend for the metals effects of trace element mixtures was found. For example, Spehar and Fiandt (1986) studied As, Cd, chromium (Cr), Cu, mercury (Hg), and Pb. Acute tests with metals mixed at multiples of the LC50 indicated that joint action was more than additive for Fathead minnows and nearly strictly additive for Daphnids. Chronic toxicity tests showed that joint action was less than additive for Fathead minnows but nearly strictly additive for Daphnids, indicating that long-term metal interactions may be different in fish than in invertebrates. In Spehar and Fiandt's (1986) study, adverse effects of As, Cd, chromium (Cr), Cu, mercury (Hg), and Pb were observed at mixture concentrations of one-half to one-third the Maximum Acceptable Toxicant Concentration (MATC) for Fathead minnows and Daphnids, respectively, suggesting that components of mixtures at or below no-effect concentrations may contribute significantly to the toxicity of a mixture on a chronic basis.

Quantitative estimation of mixture toxicity may be accomplished by addition of toxic units using the following equation:

$$A_m / A_i + B_m / B_i = S \quad \text{eq. 2}$$

where A and B are chemicals, *i* and *m* are the toxicity values (e.g., LC50s) of A and B individually (*i*) and in a mixture (*m*), and S is the sum of responses. (Marking and Dawson, 1975). The toxicity of mixtures of Cd, Pb, and Zn to various species have been reported as additive, greater than additive, or less than additive (FAO, 1980). Testing various combinations of metal at concentrations representative of typical SR levels, Bailey and Saltes (1982 b) found interactive effects of metals in SR water to be additive in general.

Addition of toxic units can be conducted using the river water metals information supplied by Pelletier (1994). In that report, Zn and occasionally Cd, posed excess risk to biota using the same aquatic life criteria. When the risk of toxicity from each of the metals is summed, the total risk is obviously greater. The total risk of metal toxicity would be greatest in December through June, during the highest annual flows.

Bioaccumulation and Biomagnification

Concentrations of contaminants in tissue provide a time-averaged assessment of contaminants as well as insight into the complexities of the fate, distribution, and effects of various contaminants (Crawford and Luoma, 1993). Thus, analyzing for contaminants in tissue can help assess the biological integrity of streams.

Some elements tend to bioaccumulate because of their chemical similarity to biologically required elements. For example, animals with calcareous skeletons, exoskeletons, or shells take up Pb to a greater extent than those without, because Pb follows similar biochemical pathway to calcium, for which these organisms have evolved a high assimilation efficiency. Because of a slower rate of elimination than of uptake, Cd can also bioaccumulate in aquatic food chains.

Biomagnification is the result of processes of bioconcentration and bioaccumulation by which tissue concentrations of bioaccumulated chemicals increase as the chemicals pass up through trophic levels. Such chemicals are transferred from food to consumer, so that residue concentrations increase systematically from one trophic level to the next. The Because Cd has a higher bioconcentration factor in most primary consumers than does Zn, predators at higher trophic levels may be exposed to a Zn:Cd ratio of less than 10 and hence be poisoned more by Cd rather than by Zn, even though Zn concentrations are greater than Cd concentrations in water.

Literature reviews have reached conclusions about tissue concentrations associated with adverse effects. For example, USFWS concluded tissue residues of 13 - 15 ug/g Cd represent a significant hazard to animals at higher trophic levels. (Eisler, 1988). Despite the tendency of these metals to bioaccumulate, no strong evidence of biomagnification has been reported in studies of SR biota. For example, Funk et al. (1973) found SR fish tissues had lower concentrations of metals than the aquatic plants, insects, or algae. Yake (1977) studied metals in tissue from Longnose suckers, brook trout and Rainbow trout taken from the Upper SR in 1975, as well as walleyes taken from the Lower SR in 1977, and concluded that substantial quantities of metals are incorporated into fish tissues but did not biomagnify. Farag et al. (1998) reached the same conclusion in a study of metals in sediments, biofilm, macroinvertebrates, and fish from the CdA River: there was no evidence of biomagnification. Conversely, the USGS 1998-1999 data support these findings since whole Caddisfly tissue metals concentrations were higher than those in Largescale sucker liver, Rainbow trout muscle, and whole-body Largescale sucker, Rainbow trout, and Mountain Whitefish samples.

Phytoplankton

Analysis of metal content in tissues of SR organisms indicated that algae were the prime concentrators of Cd, Pb, Zn, and other metals. This suggests that high metal uptake is the reason for the impairment of the SR phytoplankton productivity (discussed below in the Primary Productivity Assessment section). Algae and detritus consumers such as *Hydropsyche* larvae and *Baetis* nymphs were found to have high metal concentrations, yet most higher aquatic plants showed relatively lower concentrations (Funk et al, 1973).

Macroinvertebrates

Bioaccumulation of metals by macroinvertebrates would be significant if populations of these species, or species that depend upon them as food (such as many game fish), were harmed. In his study of the lower SR, Kleist (1987) examined the stomach contents of Rainbow trout, revealing that this species feeds predominately on *Hydropsychidae*

(Caddisflies) (46.2% of diet). In 1999, USGS collected and analyzed metals data on Caddisflies from all five of the USGS sites between Seven Mile (RM 63) and the State Line (RM 98.7) (Maret and Dutton, 1999). Figure 5 shows the results of this effort. Caddisfly trace element data are also listed in Table 7.

Table 7. Trace elements in Caddisfly tissue from sites on the Spokane River, July 1999

	Site location					
	Otis		Trent- wood	Green	7 Mile	
	Post Falls	Orchards				
RM	100	96	90	85	77	63
As	2.2	2.4	3.4	3.6	2.9	2.0
Cd	3.3	3.5	3.2	3.3	3.0	1.7
Pb	45	52	53	92	47	20
Zn	450	500	530	550	520	330
% moisture	90	83	78	83	80	83

Note: Concentrations in ug/g dry weight.

Figure 5. Caddisfly trace element data, Spokane River, 1999

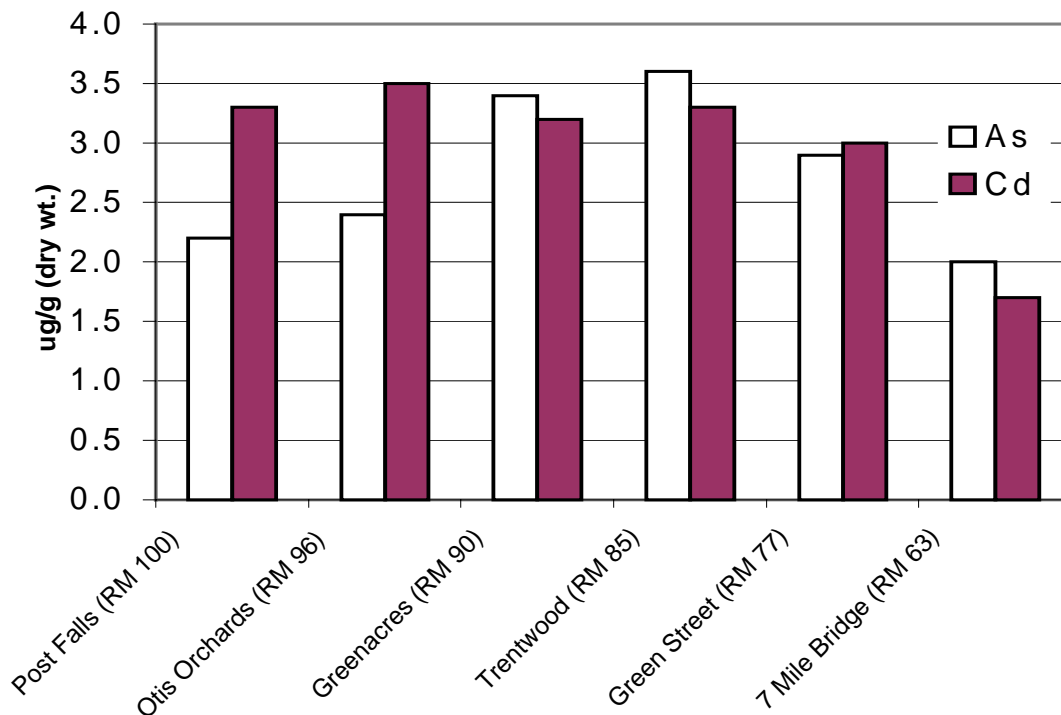
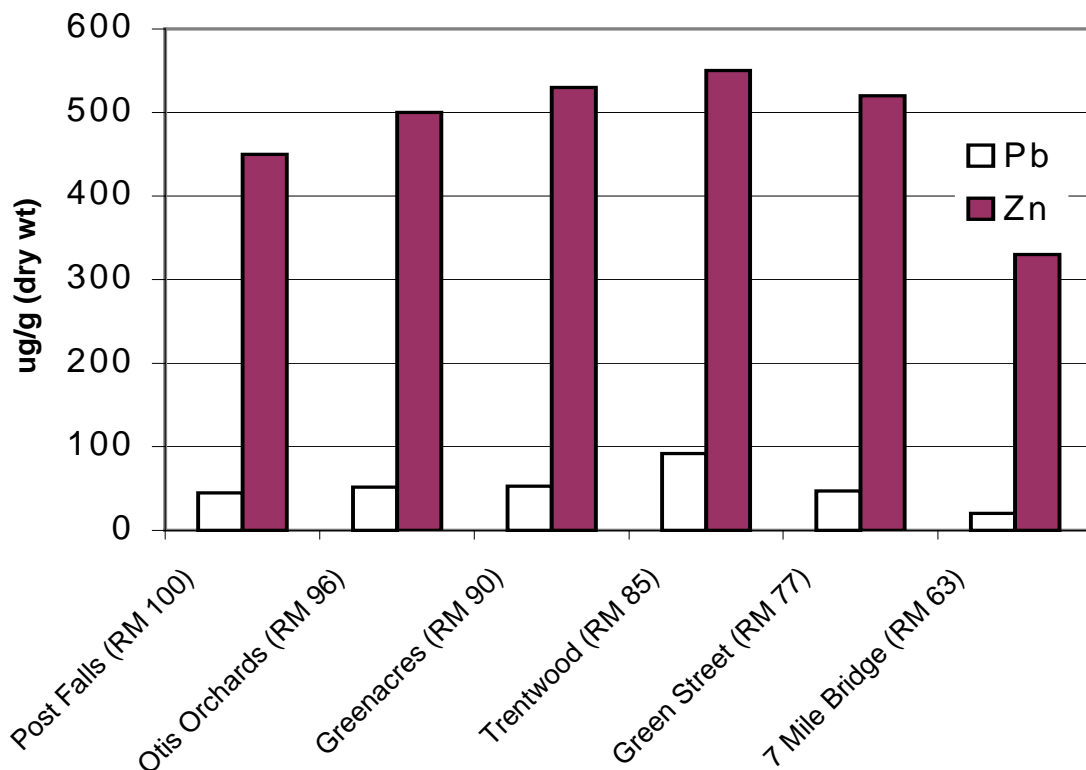


Figure 5. (continued)



Caddisflies were collected during July 1999 from six sites along the SR, from RM 100 - to RM 63, by the USGS, who reported the metal concentrations in composite tissue samples of these abundant invertebrates (USGS 2000). Caddisfly composite samples from metal contaminated reaches of the Clark Fork (RM 350 - 490) (1986-1996) and Spokane-CdA Rivers (RM 100 - 195) (1994), reported by Maret and Dutton (1999). For comparison of Caddisfly tissue metals concentrations between these rivers, Table 8 shows the mean metal concentrations in Caddisfly composite samples from the Clark Fork and CdA Rivers, reported by Maret and Dutton (1999), and the SR, reported by the USGS (2000). Means are the averages of at least five composite samples taken at sites along each river.

Table 8. Mean metal concentrations in CdA, Spokane, and Clark Fork Rivers Caddisfly composite tissues.

	Cd	Pb	Zn
Upper Spokane-CdA¹ R.	19.3	565.0	1483
Spokane² R.	3.0	51.5	480
Clark Fork¹ R.	1.2	5.6	193

Note: Mean metal concentrations (ug/g dry wt.) of >5 composite samples from each river

Sources: ¹Maret and Dutton, 1999

²USGS, 2000.

Nimmo and Castle (1998) found that macroinvertebrate tissue-metal concentrations of 172 ug/g of Zn (dry wt.) appeared to be detrimental to the macroinvertebrate community of a metals contaminated stream, compared to a reference stream not influenced by mining. This is consistent with effects seen in the SR, which has even greater tissue Zn levels in macroinvertebrates.

During July 1999, metals in Spokane River Crayfish were estimated by Johnson (2000) by analysis of single composites from three reaches, of three to five animals each. The sites were Plante Ferry, Green Street, and Seven Mile Bridge. The whole body burdens of Cd, Pb, and Zn in the Crayfish decreased progressing down stream. Figure 6 depicts the estimated dry weight metal concentration, based on an estimate of 75% moisture content in the reported wet weight results.

Figure 6. Metals in Whole fish and Crayfish, Spokane River, July 1999

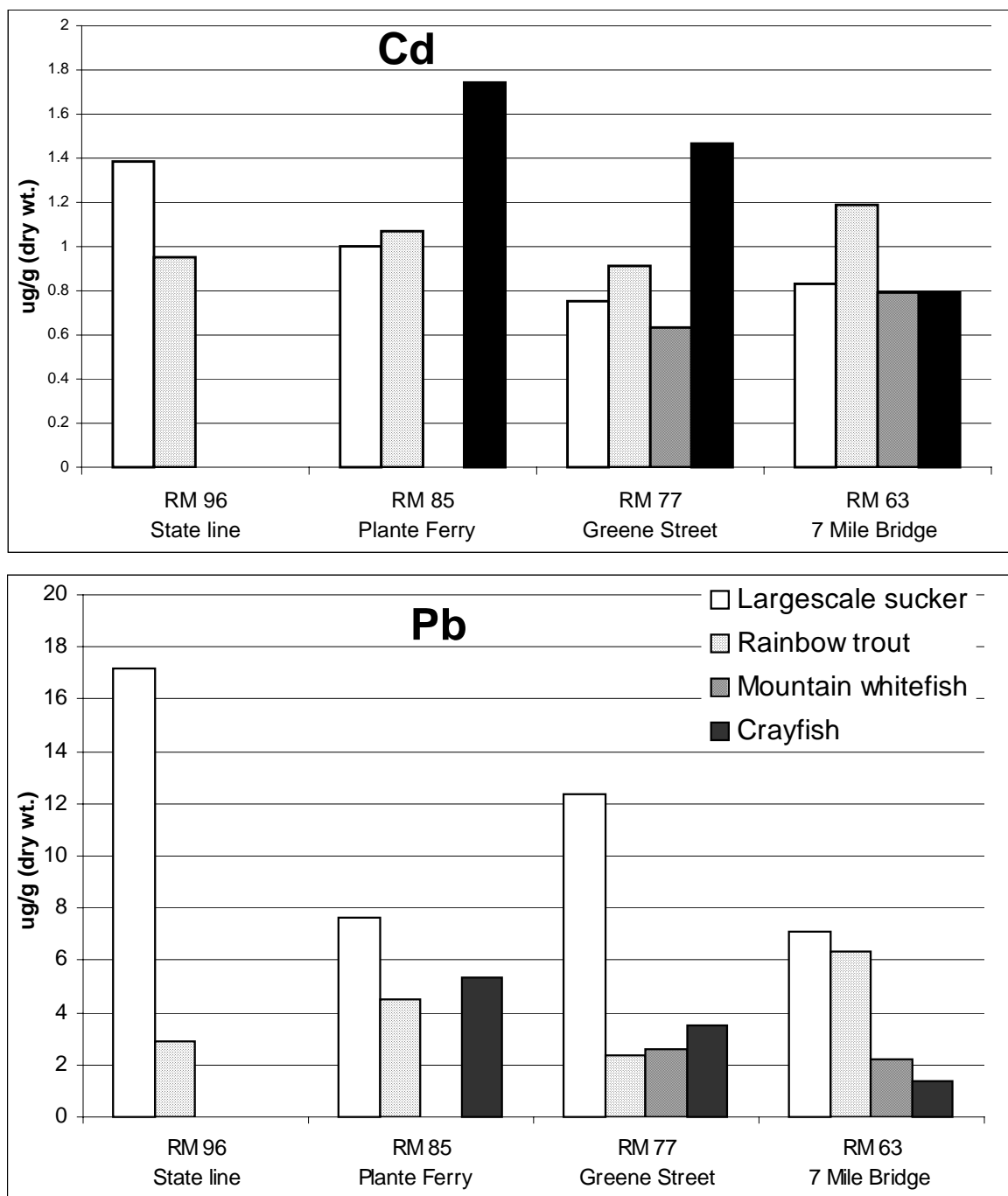
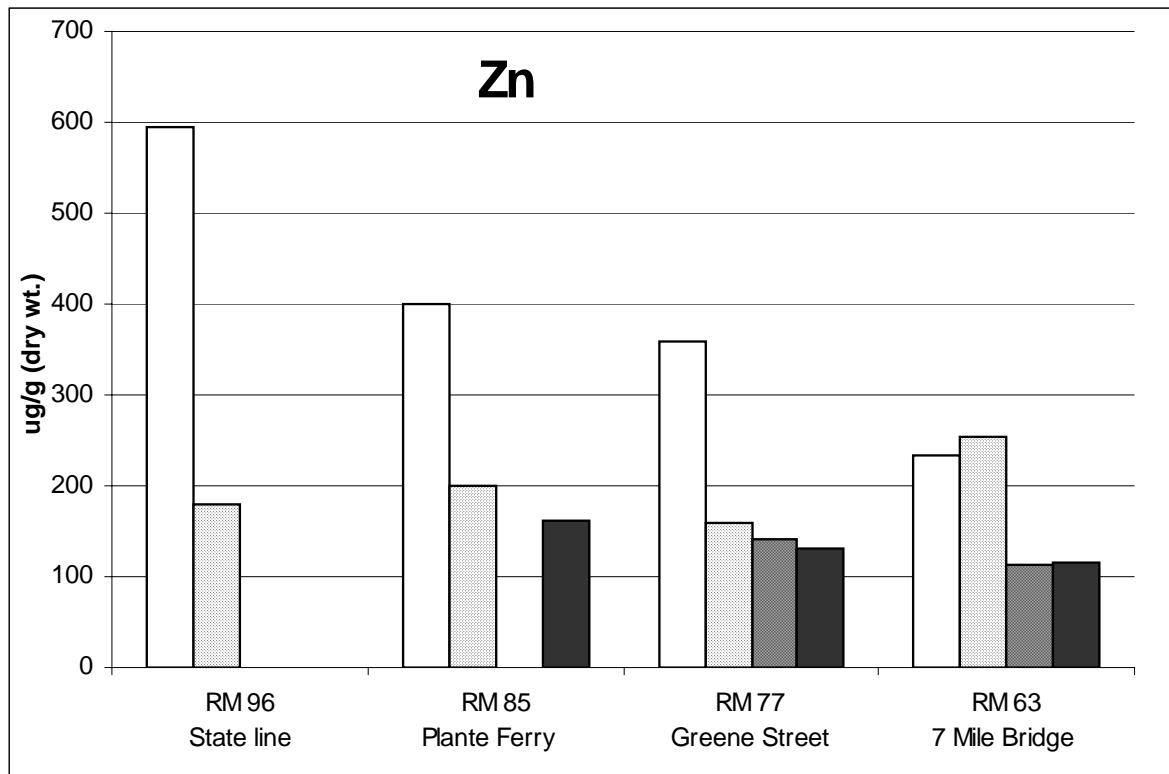


Figure 6. continued



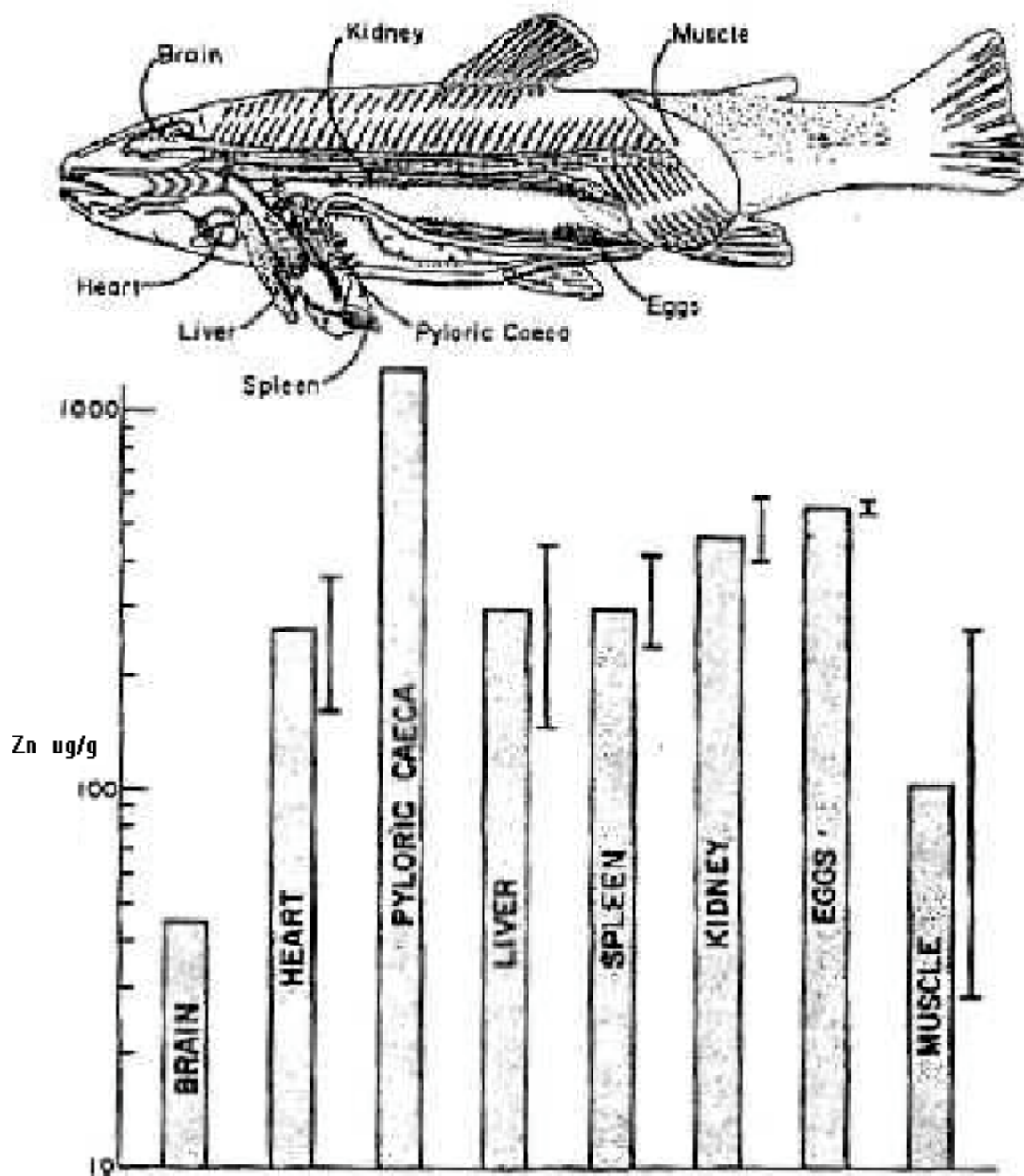
Fish Tissues

Fish as well as macroinvertebrate tissues have been used to evaluate trace element contamination in streams affected by mining wastes (Hattum et al. 1991; Moore et al., 1991; Hornberger et al. 1997; Farag et al. 1998).

Relative to primary producers and macroinvertebrates, analysis of tissues of various SR biota has shown a considerably lower concentration of metals in fish than in aquatic plants, insects, or algae (Funk et al. 1973). Funk et al. (1973) measured Zn at concentrations of 80-200 mg/kg in liver tissues of several fish species. Skeletal muscle tissues generally contained less than one-quarter of these amounts. Mean Zn concentrations in fillet tissues were 33, 55, and 54 mg/kg in the Perch (*Perca flavescens*), Bullhead (*Ictalurus melas*), and Squawfish (*Ptychocheilus oregonensis*), respectively. Funk et al. (1975) reported that fish from the SR had Zn levels about 200 mg/kg. The relative accumulation of Zn by different tissues is shown in a figure borrowed from Funk et al. (1975): Figure 7. Zn levels in pyloric caeca were approximately six-fold higher than in liver, and were the lowest in muscle and brain tissues (Figure 7).

Saltes and Bailey (1984) reported metals analysis of fish collected in 1972, 1980, and 1981 from the SR between Post Falls Dam (RM 102) and (RM 80.2). Gill and liver tissue were analyzed for Zn. Zn bioconcentration factors of 9708-fold for gill and 3835-fold for liver tissue were found.

Figure 7. Relative Zn accumulation by different tissues in fishes of the Spokane River



Source: Funk et al., 1975

Composite samples of whole Largemouth suckers, and sport fish fillets were collected from five reaches of the SR between Lake CdA and Lake Roosevelt (Johnson et al. 1994). Significant contamination by Cd, Pb, and Zn was found. Most whole fish samples had high concentrations of those metals. However, metal concentrations were near detection limits in the majority of fillet samples, except for the area above (RM 80.2). Fillets from Rainbow trout collected at this site had elevated Pb concentrations of 0.49-0.75 ug/g, compared to 0.059 ug/g or less in fillets collected elsewhere.

In 1998 and 1999, USGS collected fish from various sites between the state line (RM 98.7) and Seven Mile (RM 63). They determined metals concentrations in Rainbow trout muscle and Largemouth sucker liver tissues. No whole-body composite tissue samples were analyzed. The results for the Rainbow trout samples collected in 1998 are shown in Table 9.

Table 9. Average Rainbow trout skeletal muscle tissue metal concentrations – 1998 sample at Seven Mile

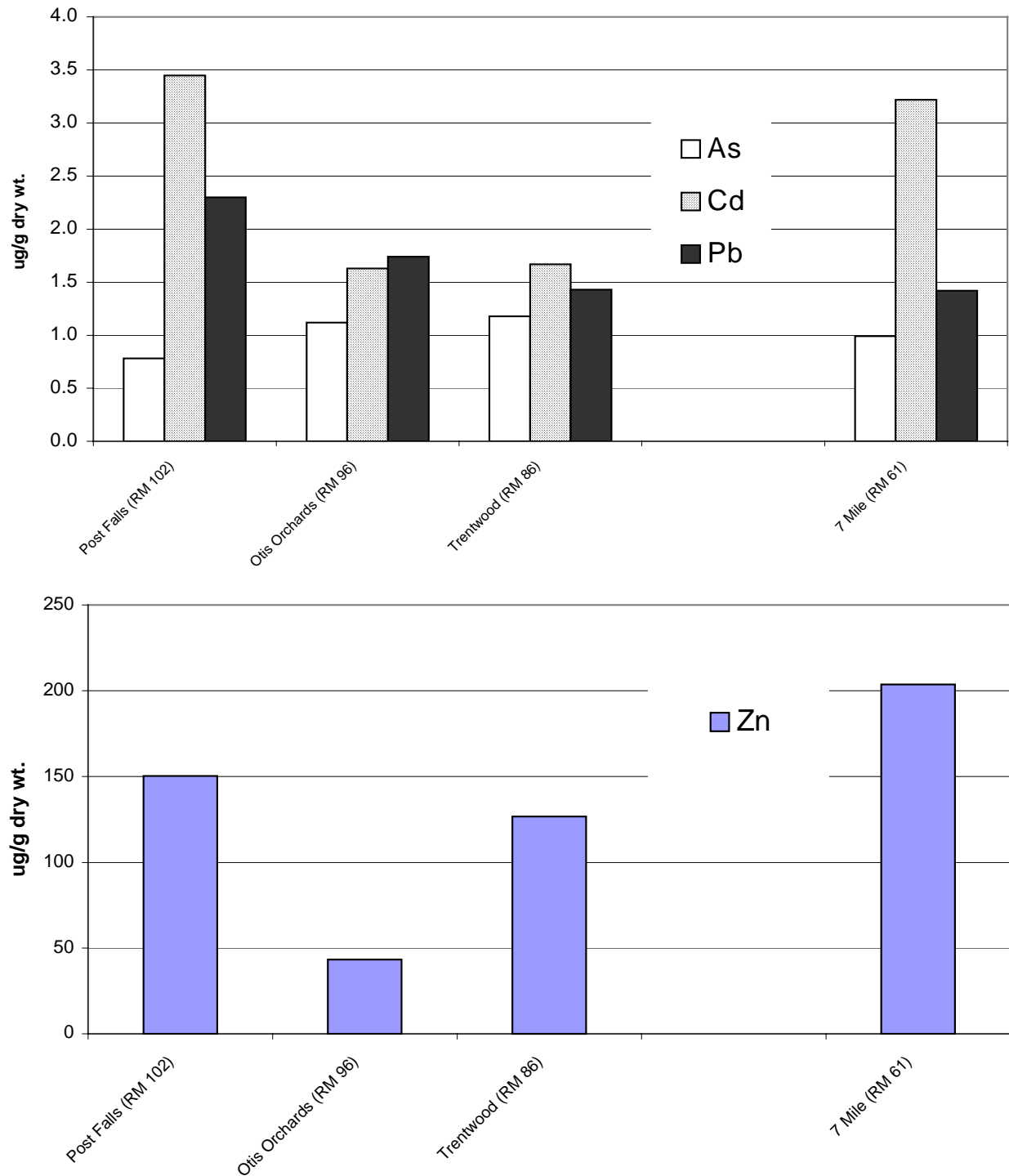
	ug/g (dry wt.)
As	nd*
Cd	nd*
Pb	0.83
Zn	22.7

*nd = not detected, Reporting limit 0.1 ug/g (dry wt.)

Note: Samples were fillets with skin removed

In Figure 8, the results of the USGS Largescale sucker liver monitoring done in 1999 are shown.

Figure 8. Largescale sucker liver metals from sites on the Spokane River, July 1999.



The Largescale sucker liver and Rainbow trout tissue analyses are also given in Table 10.

Table 10. Average metal concentrations* in Largescale sucker livers from the Spokane River, 1998-1999

	Reporting limit	Site			
		Post Falls (RM 102)	Otis Orchards (RM 96)	Trentwood (RM 85)	7 Mile Bridge (RM 63)
		July 12, 1999	July 27, 1999	July 28, 1999	Aug 5, 1998
As	0.1	0.78	1.12	1.18	0.99
Cd	0.1	3.45	1.63	1.67	3.22
Pb	0.1	2.30	1.74	1.43	1.42
Zn	0.5	150.29	43.36	126.74	203.69
percent water		74.60	69.83	74.39	77.49

*ug/g dry wt., unless noted otherwise.

Whole body metals levels in Largescale suckers and Rainbow trout were determined by Johnson (2000) in an analysis of multi-animal composite tissues of each species, from State Line, Plantes Ferry, Green Street, and Seven Mile Bridge SR reaches during July 1999. Two Mountain whitefish, one from Green Street and one from Plant Ferry, were also analyzed. Unlike the crayfish Johnson analyzed, the whole body burdens in the fish did not show any longitudinal concentration pattern, except for Zn, which progressed from higher to lower moving down stream. The dry weight tissue metal content was estimated from the wet weight results reported by Johnson (2000). Fish tissue moisture contents average approximately 75%, so this figure was used as a conversion factor. It was within < 1% of the percentage of tissue water content in fish reported in the 1999 USGS SR fish study. Figure 6 depicts the estimated dry weight tissue metal concentration for the individual whole fish from the Johnson (2000) study.

A search of scientific literature identified few studies with data on adverse effects of metals with corresponding reports of tissue metals concentrations. Dixon and Sprague (1981) exposed immature Rainbow trout for 21 days to As. They did not exhibit effects on growth despite achieving whole body tissue levels of 3 ug/g. Using immature Brook Trout (*Salvelinus fontinalis*) Hamilton et al. (1987) found no correlation between metallothionein concentration and mortality or tissue residues at the lowest Cd concentration they tested (<3600 ug/L Cd), despite a significant increase in metallothionein. Beattie et al. (1978) measured whole body larval Rainbow trout Cd levels in fish at the threshold dose for mortality for 100% of exposed fish. Complete mortality of alevins occurred within 320 hours with a corresponding tissue concentration of 0.84 ug/g. In egg-embryo exposures, whole body concentrations of 0.21 ug/g were found in alevins unable to break free from egg membrane during hatching, resulting in death. The fish had deformed vertebrae, and blood clots in fins. There was no effect on growth in trout with muscle Pb at 0.6 ug/g. However, reduced embryo hatchability and reduced weight gain were observed at tissue concentrations of 4.02, ug/g Pb (Holcombe et al. 1976). Cd and Pb accumulate in the scales of fish through exposure to water (Varanasi and Markey, 1978). Sauer and Watabe

(1989) observed Zn incorporated into the calcified region of the circuli of scales following an exposure to Zn via water. The authors suggested the possibility that scales act as a protective sink for metals during exposure (Sauer and Watabe, 1989; Sauer and Watabe, 1984). Because minerals can be resorbed from scales into fish circulation during certain time periods, such as spawning, stored metals may also be released into the circulation at such times (Varanasi and Markey, 1978), thus increasing the risk of toxic effects. Holcombe, et al. (1976) exposed Brook trout embryos to Zn at various levels. A whole body tissue concentration of 22.6 ug/g affected reproduction by reducing the percentage of eggs hatching in second-generation trout. Liver tissue concentrations as high as 50 ug/g, wet weight, had no effect on survival.

USGS and WDOE also collaborated to obtain data on organochlorine bioaccumulation in fish tissues during the 1998 and 1999 sampling efforts. The results of this effort are presented in Table 11.

Table 11. Organochlorine compounds in whole Largescale suckers and Rainbow trout skeletal muscle, Spokane River, 1998-1999

		Site				
		Post Falls	Otis Orchards	Trentwood	7 Mile	7 Mile*
RM		102	96	86	63	63
Sample Date		July 12, '99	July 27, '99	July 28, '99	Aug 5, '98	Aug 5, '98
Reporting limit						
PCBs	0.050	0.270	0.500	0.310	0.140	0.210
p,p'-DDE	0.005	0.011	0.016	0.012	0.020	0.011
Lipids (%)	0.5	2.95	5.69	2.2	2.6	14
Sample wt. (g)	0.1	10	10.02	10	10.02	10.03

* Rainbow trout fillet, all other samples are whole Largescale sucker composites.

Note: concentrations in ug/g wet weight (unless otherwise noted).

These pollutants likely play roles in ecological impacts by interacting toxicologically with metals and other contaminants in the river. PCBs have been identified as contaminants of potential ecological concern in the Spokane River. These have originated from past industrial activities along the river and have resulted in elevated tissue concentrations in fish extending from above the Upriver Dam to the Spokane Arm (WDOE 1995; Golding 1996). Organic carbon normalized sediment PCB concentrations are highest behind the Upriver Dam (RM 80.6) and near RM 75.4. The WDOE (1995) reported that SR fish tissue PCB levels exceed the 0.11 ug/g wet weight guideline for protection of piscivorous wildlife, published by Newell et al. (1987). The fish tissue samples collected in 1998-1999 also exceeded this criterion at all four locations. In contrast, direct effects of PCBs on these species are unlikely at this level. For example, Hogan and Brauhn (1975) measured PCB 1242 in Rainbow trout. A whole body tissue level of 1.3 ug/g was needed to produce 10% egg mortality. Also, Poels et al. (1980) found that PCBs at 2.2 ug/g in adult Rainbow trout fat corresponded to a 40% decrease in growth relative to controls. Nonetheless, adverse effects in fish and populations of other aquatic organisms from Zn exposure may be compounded by effects from PCB accumulation.

Other chemicals from effluent point-sources and runoff non-point-sources along the SR have the potential to contribute to the aggregate ecological stress within the river. One probable aggregate stressor is DDE. Tissue levels of DDE may be high enough in some recent fish samples (Johnson, 2000) to compound the adverse physiological effects of other stressors. DDE can produce a variety of sublethal effects. For example, Poels et al. (1980) found that in adult Rainbow trout, a 35% increase in kidney size relative to controls (ED35) occurred when levels of 0.080 ug/g DDE were present in their fat. Thus DDE levels are four-fold or lower than those known to cause renal effects. Favorably, SR fish tissue DDE levels are at least five fold lower than the Newell et al. (1987) 0.12 ug/g wet weight DDE guideline for protection of piscivorous wildlife.

Interactive Effects

Elevated body burdens of metals, in conjunction with stress from other factors, can enhance adverse outcomes. Studies have shown that population sizes and structures of aquatic species can be affected by factors other than toxic chemicals. These factors include conditions such as physical habitat characteristics, food availability, and fishing pressure.

In spite of there being a great deal of information on the toxicity of metals to fish, relatively little work has been conducted on interactions with temperature, except for As, Cd, and Zn. Rainbow trout are more sensitive to acute doses of arsenate at 5°C than at 15°C, but the reverse occurs when they are exposed to chronic doses of arsenate (McGeachy and Dixon 1990). A critical body burden of arsenate must be achieved before death, which occurs more rapidly at warmer temperatures because of enhanced uptake rate. At lower concentrations (where detoxification mechanisms are not overwhelmed), elevated temperature facilitates detoxification processes and thus delays or prevents achieving the toxic arsenate body burden (McGeachy and Dixon 1990).

Zn toxicity has been reported to be unaffected or to increase at high temperatures (Cairns et al. 1975). A study by Hodson and Sprague (1975) provides an explanation: Using Atlantic salmon (*Salmo salar*), they concluded that fish are more sensitive to Zn at high temperatures when exposures are at high concentrations and of short duration. As exposure duration is extended, temperature effects are progressively reduced until, at 2-week exposures, the LC50 is higher in warm water. The phenomenon is similar to that seen with arsenate. The mechanisms for the temperature effect may not be the same, however. Acute Zn poisoning causes death by destroying gill tissue. Hodson and Sprague (1975) found that cold-acclimated fish experience more gill damage from low doses of Zn than do warm-acclimated fish; even though warm, they had greater concentrations of Zn in the gills. Whereas fish are more sensitive to arsenate and Zn at cold temperatures, Heath (1987) found that cold-acclimated (6°C) trout exhibit a threefold greater 10-day lethal threshold for Cd compared to fish at 18°C. The elevated toxicity of Cd at the higher temperature is correlated with enhanced plasma calcium suppression by Cd. Hypocalcemia is an important toxic mechanism of Cd toxicity to fish (Heath 1987). Eisler (1974) reported Cd toxicity to increase threefold at 20°C than at 5°C for Mummichog (*Fundulus heteroclitus*).

Acclimation to Metal Stress

Bailey and Saltes (1982) researched the factors contributing to the existence of what they described as a healthy salmonid population in the SR, which contained concentrations of Zn approximately 100-ug/L, at the time. Their results indicated that through physiological mechanisms, SR Rainbow trout were much more tolerant to Zn (96 hr LC50 = 1169 ug/L) than unacclimated hatchery trout (96 hr LC50 = 100 ug/L) or hatchery trout acclimated to 100 ug/L (96 hr LC50 = 170 ug/L). The 96 hour LC50 of metals to SR acclimated, and unacclimated, hatchery Rainbow trout followed the same pattern. The relatively high LC50s of SR Rainbow trout compared to unacclimated Rainbow trout indicate profound adaptation of the SR population. The relatively low bioaccumulation of these metals in SR Rainbow trout compared to SR Hydropsychids suggests that the trout population has adapted by reducing uptake or enhancing elimination of the metals, even though these Caddisflies make up a major portion of their diet. Such adaptive homeostatic mechanisms (allowing these animals to maintain internal stability) would have appreciable energy costs to this and other species that have adapted in this way.

Primary Productivity Assessment

Studies suggesting that high metals concentrations are suppressing productivity has been provided by a number of investigators. Algal toxicity tests have shown the Zn present in the SR to be inhibitory to *Selenastrum capricornutum*. The water quality of the SR was shown to be of good to excellent quality in all parameters tested except for high metal content, especially Zn (Funk et al. 1973). Analysis of metals in tissues of SR organisms indicated that the algae were the prime concentrators of Cd, Pb, Zn, and other metals. Algae and detritus consumers such as *Hydropsyche* larvae and *Baetis* nymphs had high concentrations. Most higher aquatic plants showed relatively lower concentrations. Falter and Mitchell (1982) studied the aquatic ecology of the SR between CdA and Post Falls, ID, in 1980, finding aqueous concentrations of Zn ranging from 85 – 160-ug/L, extreme inhibition of phytoplankton (in algal bioassays), and productivity in the extremely oligotrophic range. Pfeiffer (1985) collected phytoplankton in the lower SR reservoirs, finding extremely low abundance. Soltero et al. (1976) studied the water quality of Long Lake and its tributaries using algal assays. Zn concentrations ranged from 3 - 121-ug/L. Growth inhibition of *Selenastrum capricornutum*, existed in every sample from Long Lake. Addition of EDTA, which chelated the metals reduced the inhibitory effect. Greene et al. (1978) conducted similar studies along with some additional work. They concluded that high flows in the SR increased the metal concentrations found in Long Lake; that Zn was the dominant metal affecting *Selenastrum* and *Anabaena* grown in Long Lake waters; that EDTA increased growth of *Selenastrum* and *Anabaena*; and that *Spiraeroystis schroeteri*, the dominant chlorophyte isolated from Long Lake, produced its maximum yields without the addition of EDTA. These results led the authors to conclude that the indigenous phytoplankton standing crop in Long Lake was composed of Zn tolerant species (Greene et al. 1978). Soltero et al. (1981) found that Zn appeared to be inhibiting blue-green algae populations. During 1980, the seasonal mean concentrations of Zn between Spokane and Long Lake, and in Long Lake, were 141 and 45 ug/L, respectively. Zn concentrations and maximum bluegreen algal standing crop biovolume were inversely related. The Zn levels reported in these studies, and clearly linked to algal toxicity, are nearly the same as current Zn levels.

In 1999, the USGS gathered data by which primary productivity in the SR could be estimated: they measured pheophytin a, and chlorophyll a (shown in Figure 9), and ash-free dry mass in river water samples (shown in Figure 10).

Figure 9. Primary production measures - Pheophytin a, and Chlorophyll a, Spokane River, 1999

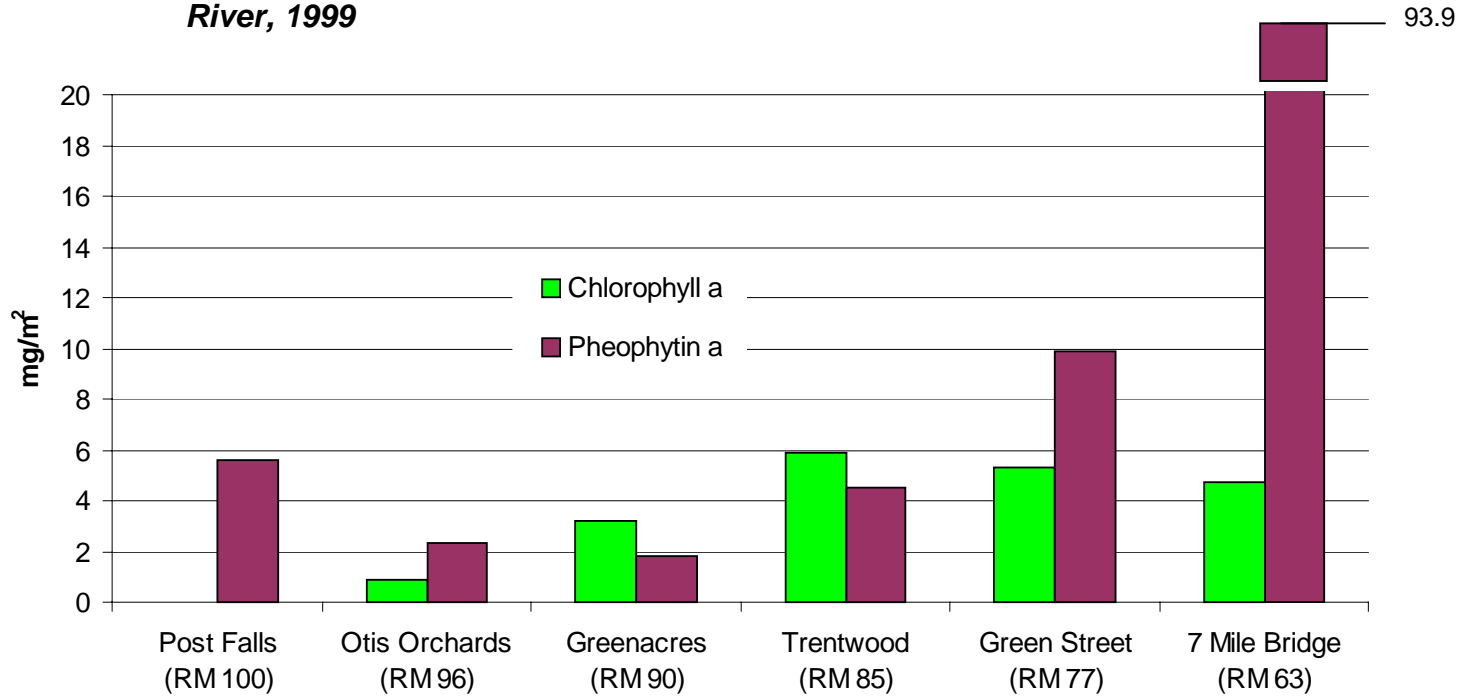
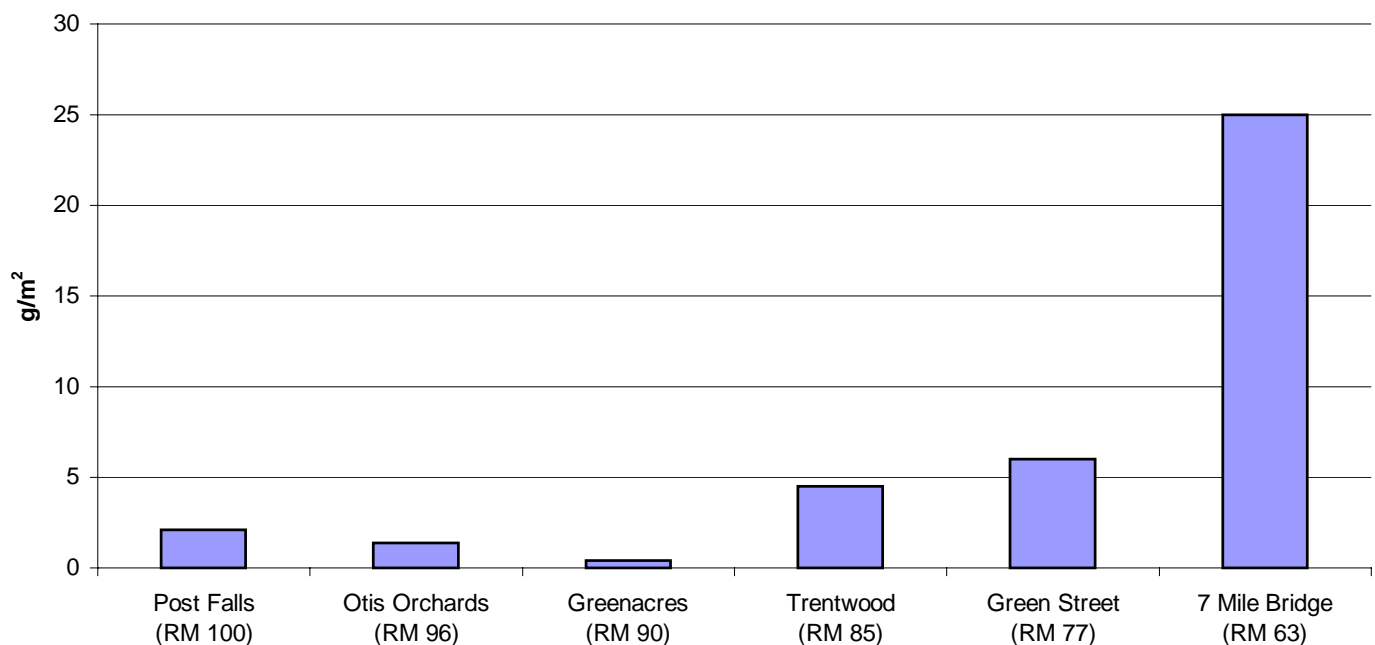


Figure 10. Ash-free dry mass of periphyton per unit surface area of riffle substrate, Spokane River, 1999



The SR is very oligotrophic until the City of Spokane WWPT outfall enters the river above the Seven Mile Bridge reach. The City of CdA WWTP might, in the absence of high river-metals concentrations, contribute sufficient nutrients (phosphorus and nitrogen) to enhance primary productivity, but no such enhancement is apparent, probably because the high concentration of Zn, and perhaps Cd and Pb, inhibit the growth of algae.

Macroinvertebrate Community Assessment

Contaminants can influence the species richness and composition of aquatic life in streams. To assess the temporal or spatial extent of effects from adverse water quality conditions on substrate dwelling invertebrate populations in the field, one may determine the population size and structure in the affected water body and compare the results to "healthy" populations.

SR macroinvertebrate populations have been examined by several investigators in the past. Unfortunately, these studies have seldom included evaluations of uncontaminated reference streams. Gibbons et al. (1984) found dense populations of macroinvertebrates in the upper river area (RM 95.1 - 72.7), in monitoring conducted between 1979-81. Some species of macroinvertebrates and fish were absent in the upper study area, leading the authors to speculate this was due to high Zn concentrations. Pfeiffer (1985) collected data on benthos, as well as fish and plankton populations. He also assessed substrate and shoreline conditions in the reservoirs of the lower SR. Kleist (1987) found macroinvertebrate communities were dominated by *Hydropsyche* and *Baetis* species with maximums occurring below the City of Spokane WWTP.

Any directly measurable effects of metals on macroinvertebrate community structure, downstream from the City of Spokane, are obscured by inputs from Hangman Creek (RM 72) and the City of Spokane WWTP (RM 67). Kleist (1987) noted downstream increases in composition and abundance of benthos and zooplankton coincide with point sources of inflow that likely contain increased amounts of nutrients or particulates. He stated that the first notable increase of macroinvertebrates occurred below the confluence of Hangman Creek. The Hangman Creek drainage basin includes large areas of cultivated land and likely contributes nutrients from agricultural runoff, and may contribute to the increased abundance observed.

The most prominent increase in both numeric abundance and biomass was below the Spokane WWTP, where effluent containing suspended organic particulates useable by *Hydropsychidae*, enters the river. Hydropsychids were represented in quantities per square meter two times higher than any station upstream and constituted about 82% of the total biomass at that station. Beyond the WWTP outfall sample station, relative values decrease but remain well above all upstream stations. The decrease may have been a result of utilization of nutrients, deposition, and/or dilution of the particulates. Macroinvertebrate abundance data for the SR were gathered by USGS in 1999. These data are summarized in Table 12.

Table 12. Riffle-dwelling macroinvertebrate taxa, Spokane River, July 1999

Taxa	Site					
	RM	Otis				Green
		Post Falls	Orchards	Greenacres	Trentwood	Street
		100	96	90	85	77
						63
<i>Acari</i>		23.2	40		80.8	11.2
<i>Asellidae</i>		23.2				
<i>Baetidae</i>		899.2	1148.8	657.6	2687.2	873.6
<i>Brachycentridae</i>		23.2				
<i>Chironomidae</i>		346.4	664	498.4	2902.4	1915.2
<i>Coenagrionidae</i>						0.8
<i>Crangonyctidae</i>						0.8
<i>Elmidae</i>				13.6		11.2
<i>Glossosomatidae</i>				53.6	107.2	11.2
<i>Hydropsychidae</i>		5692	3830.4	2862.4	3628.8	974.4
<i>Hydroptilidae</i>		92	80.8	120.8		
<i>Leptohyphidae</i>		23.2		53.6		
<i>Nematoda</i>					27.2	16
<i>Oligochaeta</i>		23.2				
<i>Planorbidae</i>		23.2				
<i>Psychomyiidae</i>						56
<i>Physidae</i>				0.8		
<i>Pyrilidae</i>			40	27.2	0.8	
<i>Rhyacophilidae</i>					3.2	13.6
<i>Simuliidae</i>		552.8	765.6	564		44.8
<i>Tipulidae</i>			20.8	28	188.8	292
Total		7721.6	6590.4	4880	9626.4	4203.2
						5743.2

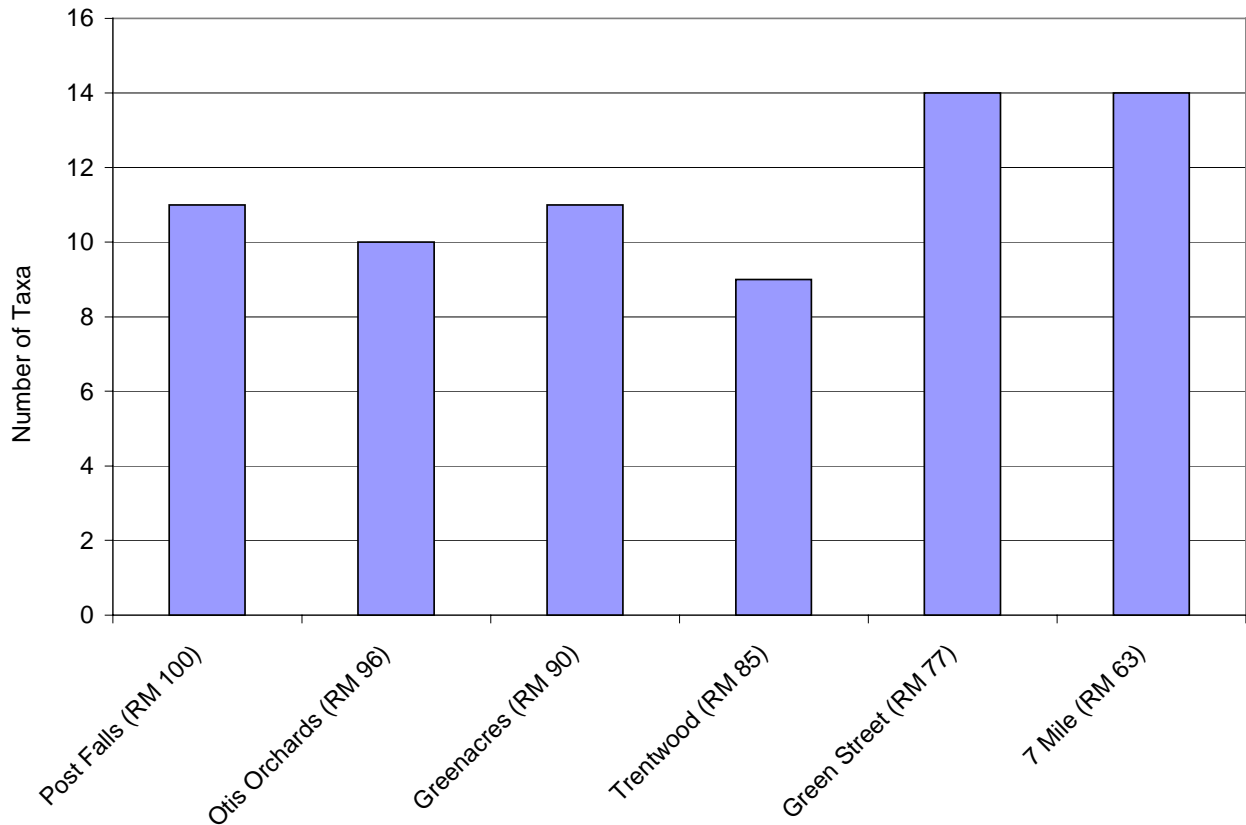
Note: Sum of Densities are abundances per square meter.

No trend in the sums of densities across stations is evident in these data, collected by USGS. However, the other data analyses revealed trends. The data are analyzed here using three metrics: Taxa richness; Ratio of *Ephemoptera*, *Plecoptera*, *Trichoptera* to *Chironomidae* abundances; and Percent dominant family contribution to total abundance.

Taxa Richness

Taxa richness reflects health of the community through a measurement of the variety of taxa (total number of families) present. Taxa richness generally increases with increasing water quality, habitat diversity, and habitat suitability. The taxa richness of samples collected by USGS in 1999 of the SR are shown in Figure 11.

Figure 11. Number of Taxa, Spokane River, 1999

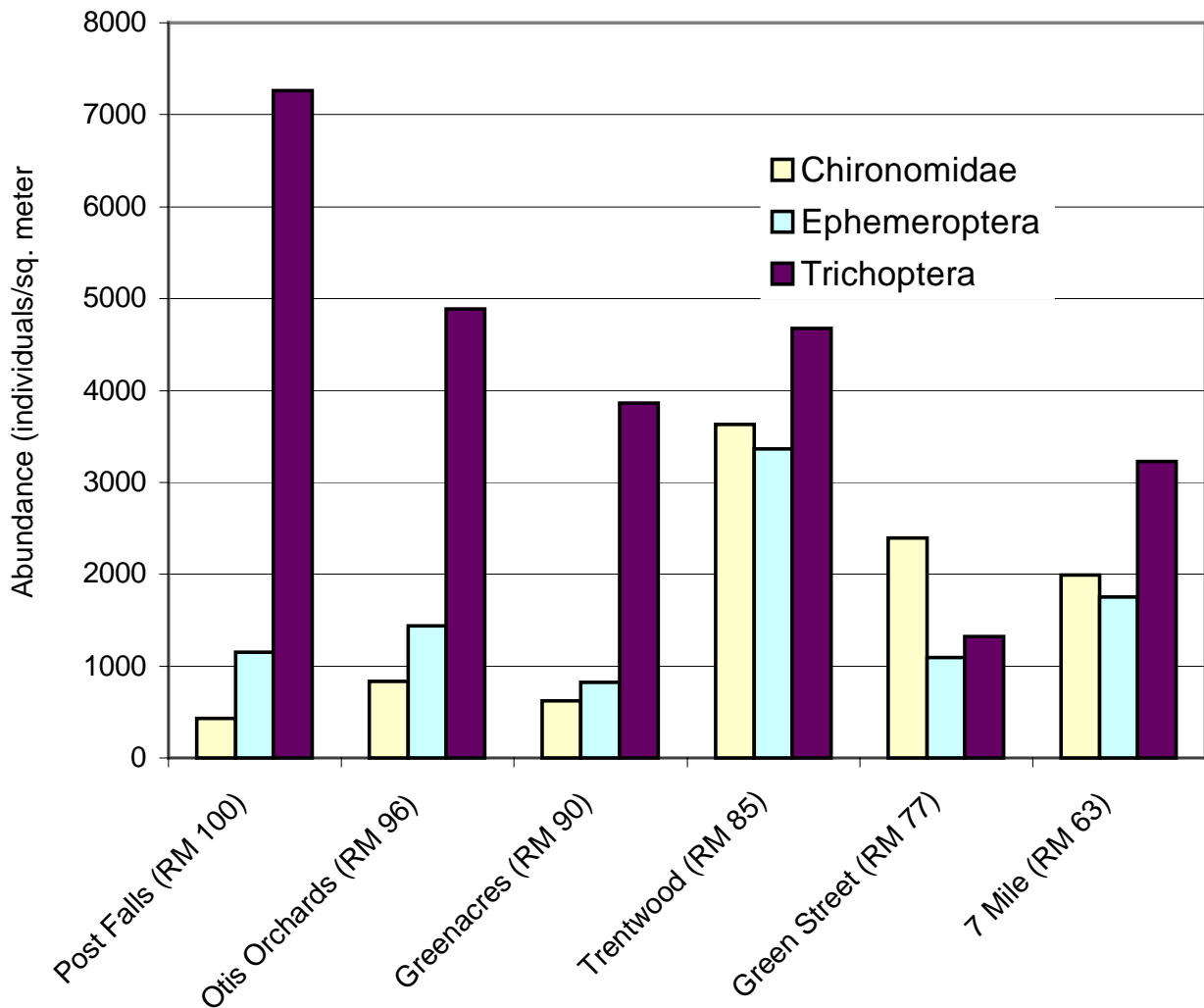


Taxa richness trends downward from Post Falls to Trentwood, groundwater recharge of the river takes place in the Trentwood reach, and a corresponding increase in taxa richness occurs. Taxa richness attains its highest level at Greenacres and Seven Mile.

Ephemoptera, Plecoptera, Trichoptera, and Chironomidae Abundance

Macroinvertebrate abundance data for the SR were gathered by USGS in 1999 (USGS 2000). The abundance of Ephemoptera, Trichoptera (EPT) and Chironomidae in the SR are shown in Figure 12.

Figure 12. Ephemeroptera, Trichoptera, and Chironomidae abundance in the Spokane River, 1999



No Plecoptera (Stoneflies) were present in the samples. The absence of this taxon is a serious ecological imbalance. The density of Hydropsychids (a genus within the Trichoptera) decreases relative to other taxa in observations progressing downstream.

As a measure of community balance, the EPT and Chironomidae abundance ratio uses relative abundance of the indicator groups Ephemeroptera, Plecoptera, Trichoptera, and Chironomidae. Good biotic condition is reflected in communities with an even distribution among all four major groups and with substantial representation in the sensitive EPT groups (Plafkin et al. 1989). Typically in this metric, Chironomids become increasingly dominant in the taxonomic composition and relative abundance compared to the more sensitive insect groups, along a gradient of increasing metals concentration or enrichment (Ferrington 1987). Numbers of Chironomidae genera have been reported to increase in response to metal contamination (LaPoint, et al. 1984). For example, Pascoe et al. (1994) compared the numbers of Chironomid genera among sites on the Milltown Reservoir and Clark Fork River,

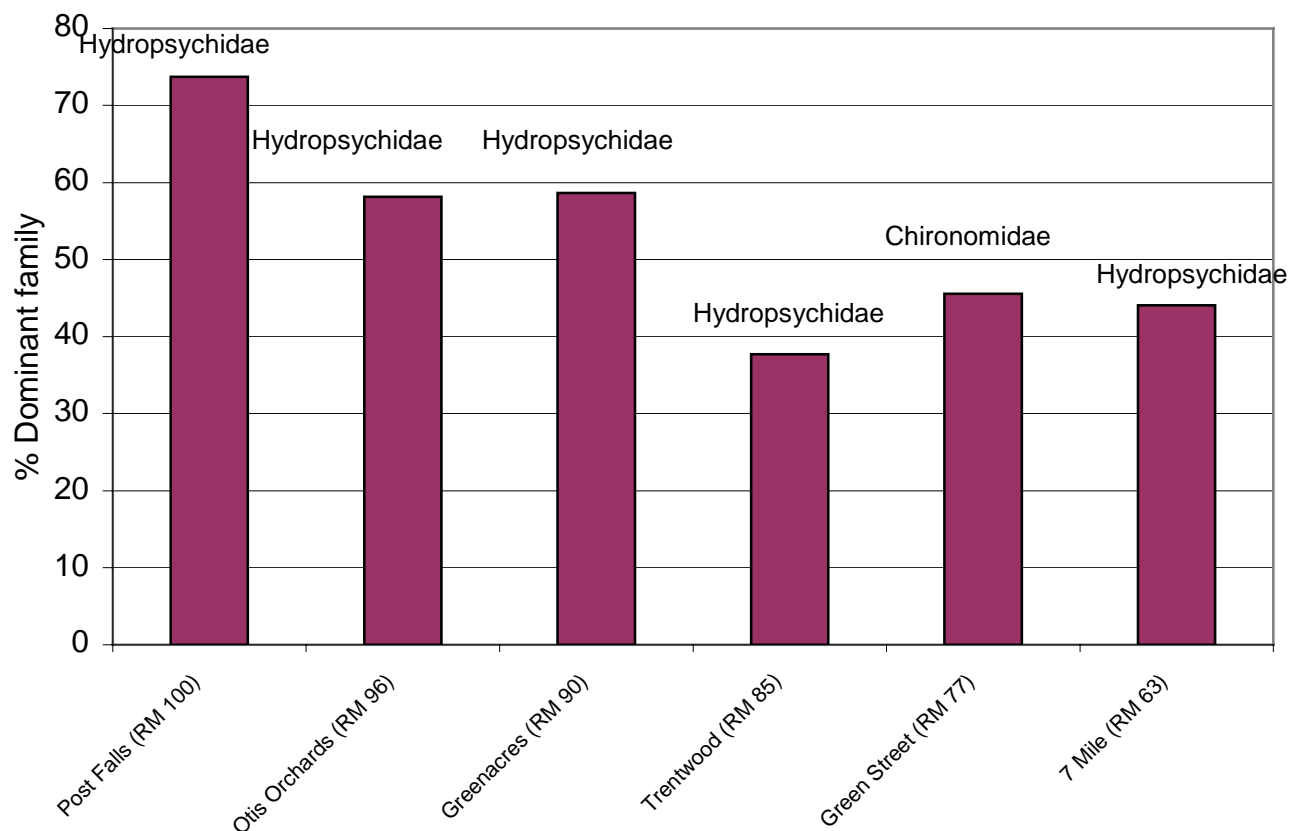
MT, based on dissolved Cu and Zn in pore water. In that study, two reference areas were compared to several metals contaminated sites. The reference areas had three and seven Chironomid genera each, whereas with 14 or more Chironomid genera, the metal contaminated sites were found significantly poorer in this benthic ecology impact metric. A similar pattern is evident in the SR samples.

The evenness amongst the other three groups improves beginning at Trentwood (where recharge from the aquifer occurs) and proceeding downstream. The improvement in abundance is probably due in large part to improving water quality progressing downstream, where contaminant metal concentrations are lower during certain seasons of the year.

Percent Contribution of Dominant Family

Figure 13, presents the macroinvertebrate community data in the context of another metric: percent contribution of dominant family. The percent contribution of the dominant family to the total number of organisms uses the abundance of the numerically dominant taxon relative to the rest of the population as an indication of community balance at the family-level. A community dominated by relatively few families would indicate environmental stress (Plafkin et al. 1989).

Figure 13. Contribution of dominant family to total abundance in the Spokane River, 1999



Hydropsychidae families were dominant in all samples except in the Green Street reach, where Chironomid families were dominant. The balance of this metric improved proceeding downstream.

Typical morphological deformities, involving malformations of mouth parts, particularly the mentum, have been reported in Chironomids. Scientific literature reveals a strong correspondence of rates of deformities with environmental pollution. These mouth part deformities are teratogenic in nature, resulting from environmental exposures during development of eggs or juveniles. Although Chironomid deformities have not been linked to specific environmental agents, the literature generally reveals the presence of metals in the suite of pollutants to which the organisms were exposed. Deformity rates, sediment metal concentrations, and metal body burdens have been examined in larval Chironomid populations from the CdA and Spokane Rivers (Moore et al., 1996). In that study, conducted during 1993 through 1995, the authors found elevated concentrations of metals and elevated rates of mouth part deformities in Chironomid larvae from the CdA River and the Idaho portion of the SR, compared to populations from other local water bodies unimpacted by metal pollutants.

Fish Community Assessment

To assess the temporal or spatial extent of effects from adverse water quality conditions on fish populations in the field, one may determine the population size and structure in the affected water body and compare the results to "healthy" populations (Farag et al. 1994). Because the river has been stocked with game fish many times, and dammed in four reaches, there is no readily available way to assess impairment to the fishery of the Spokane River. In addition, little data on comparable rivers is available.

Bailey and Saltes (1982 a) provided information regarding the SR trout population: species and age structure, total species composition, salmonid food habits, angler harvest, and minimum flow recommendations. During 1980 – 1981, direct counts of fish by snorkeling found an average of 17.9 salmonids per counter mile from Post Falls (RM 102) to Sullivan Road (RM 87.6), which were primarily of Rainbow trout. The count from Sullivan Road to RM 86.6 was 384.6 salmonids per counter mile, composed of equal numbers of Rainbow trout and Brook char. From RM 86.2 to RM 84.7 the count was 75.1 fish per counter mile, composed of equal numbers of Rainbow trout and brook char. From RM 84.7 to RM 80.2 (Upriver Dam) the count was one fish per counter mile. About 75% of the salmonid population in the upper SR were found to reside between Barker Road and Plantes Ferry.

Pfeiffer (1985) provided baseline information on the fisheries of the lower SR reservoirs, but did not contrast the survey with data from healthy fisheries. Kleist (1987) assessed the fishery of the lower SR, between Monroe Street Dam (RM 74) and Nine Mile Falls Dam (RM 58.1) via macroinvertebrate food-base composition and abundance; composition and relative abundance of existing fish populations; diet, age, and growth of salmonid species; and habitat characters. The author noted that all Rainbow trout sampled were healthy, and contained substantial amounts of body fat. Rainbow trout dominated the catch in the lotic portion while Bridgelip suckers were the predominant species in the reservoir. The Rainbow trout sample was dominated by 2+ and 3+ aged fish. Annual growth increments appeared to be somewhat less than those found in the Snake River, WA, but at- or greater than growth comparisons made nationally. Habitat indicators suggested that the lower SR provided marginal-to-good habitat for juvenile and adult salmonids, but appeared to be extremely limited in spawning habitat. Kleist also noted that Nine Mile Reservoir provided

excellent shoreline cover but bottom substrate was composed principally of silt and sand, and thus provided poor conditions for most game fish.

Bennett and Underwood (1988) assessed Rainbow trout abundance, mortality rates, seasonal distribution, movement, spawning and rearing habitat, and recruitment for the Idaho section of the SR. Their work indicated the population suffered high mortality (70% with only 10% attributed to fishing). They suggested recruitment was insufficient and that high metals concentrations were the probable cause, either alone or in combination with other likely causes, i.e., low stream flow and high temperatures ($>23^{\circ}\text{C}$). Johnson (1997) stated that the population of Rainbow trout, between Post Falls (RM 102) and the Centennial Trail Bridge (RM 84) declined in the decade preceding his study of habitat and other factors that affect recruitment. He suggested the population could be improved by increasing stream flow to keep redds covered until after fry emergence. No consideration was given to the effects of contaminant metals.

The USGS collected fish using electrofishing methods in several locations on the SR in 1998 and 1999, in order to give qualitative estimates of species composition. Different levels of effort were used at each site, therefore quantitative species abundance estimates are not possible. The fish were counted and taxonomically identified. The species composition is shown in Figure 14.

Figure 14. Fish community, Spokane River, 1998 and 1999

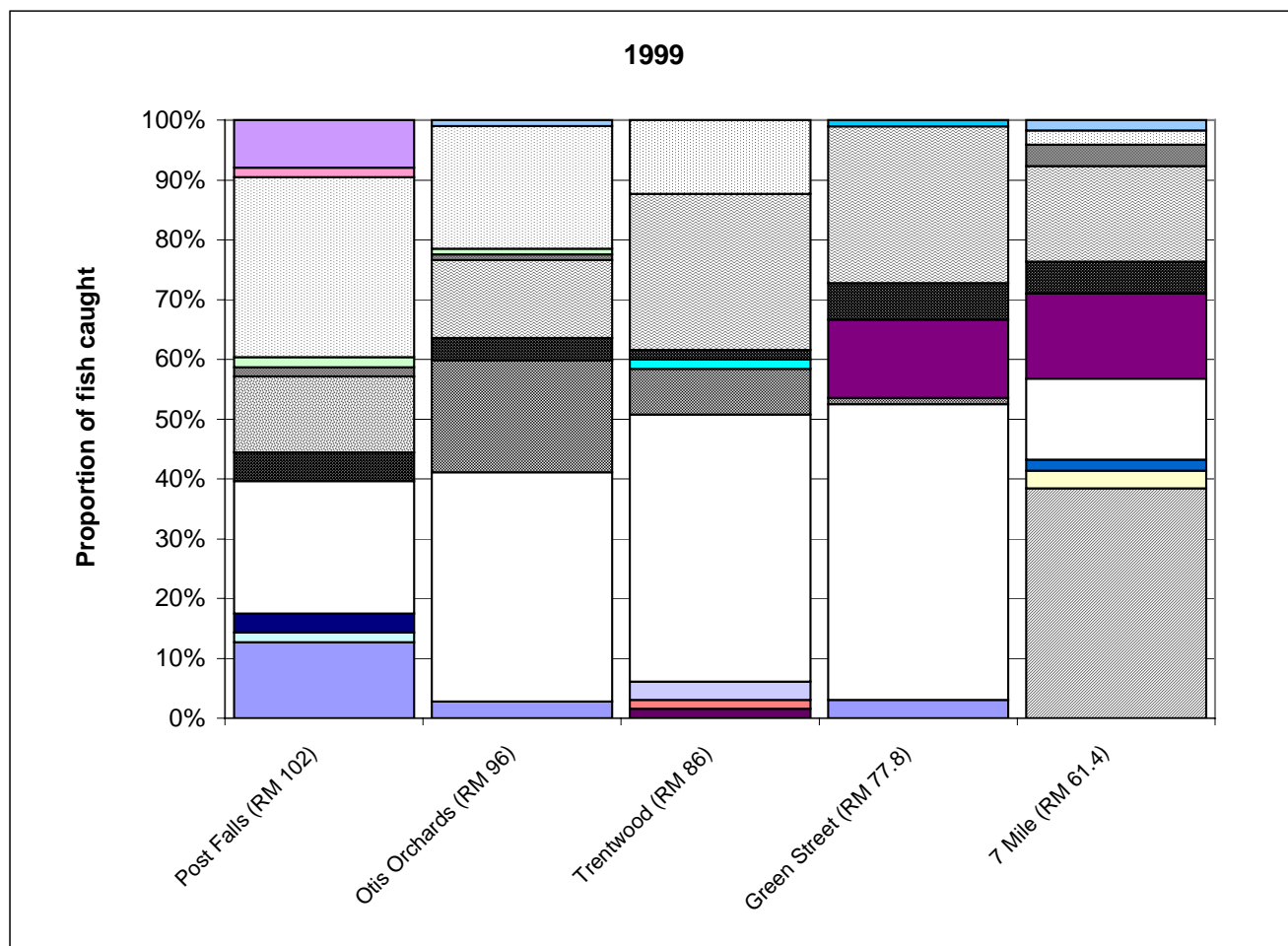


Figure 14. Fish community, Spokane River, 1998 and 1999 (continued)

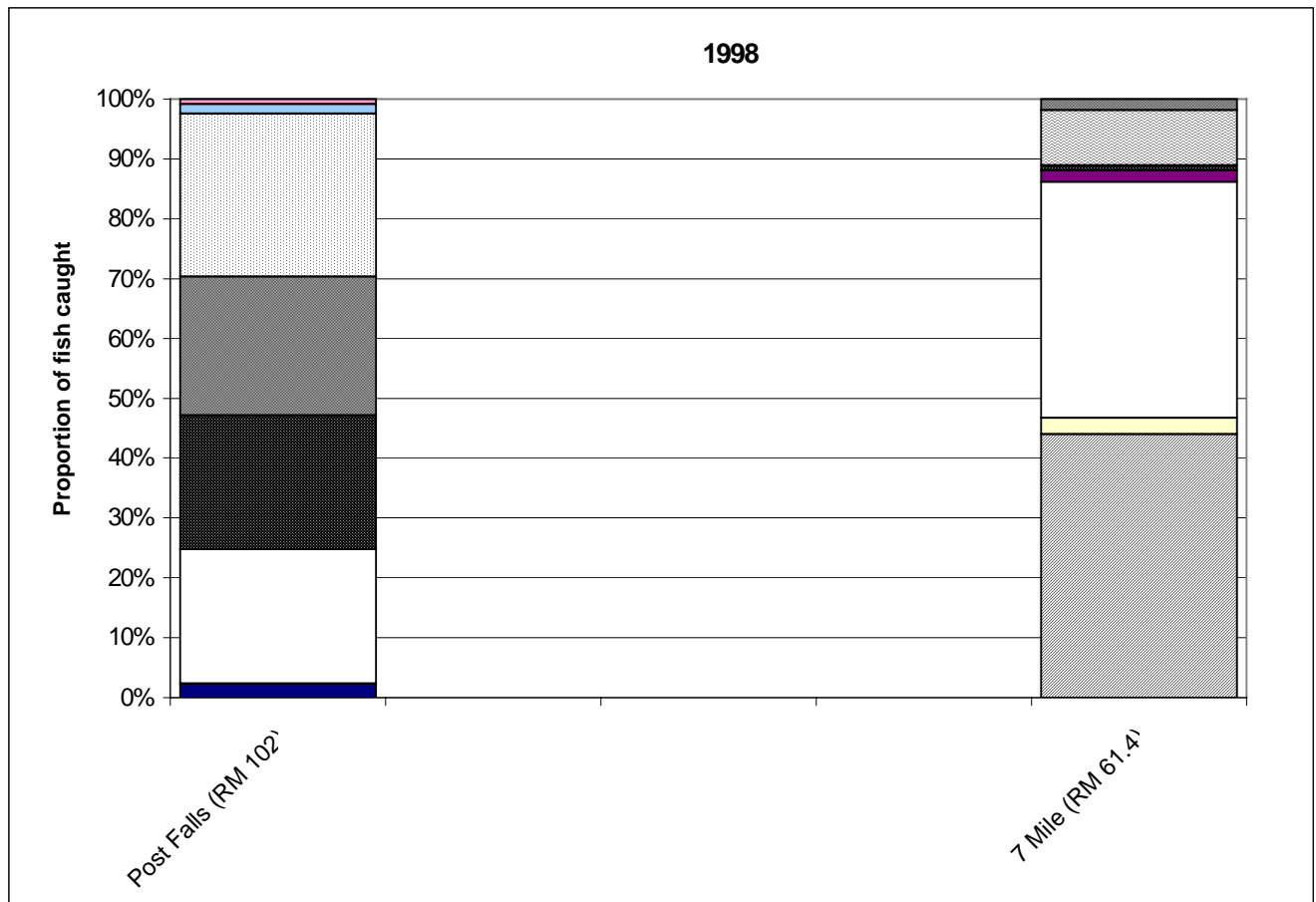


Figure 14. Fish community, Spokane River, 1998 and 1999 (legend)

-  Yellow perch
-  Yellow bullhead
-  Torent sculpin
-  Speckled dace
-  Smallmouth bass
-  Redside shiner
-  Rainbow trout x Cutthroat trout
-  Rainbow trout
-  Pumpkinseed
-  Northern pikeminnow
-  Mountain whitefish
-  Longnose sucker
-  Longnose dace
-  Largescale sucker
-  Largemouth bass
-  Cutthroat trout
-  Chiselmouth
-  Chinook salmon
-  Brown trout
-  Brown bullhead
-  Bridgelip sucker x Largescale sucker
-  Bridgelip sucker
-  Black crappie

The relative abundance of Rainbow trout increases proceeding down stream through free-flowing reaches until the Seven Mile reach, where the Long Lake pool begins and species more tolerant to poorer conditions become dominant. These results suggest that high metals concentrations effect fish species composition in the river, and that this effect can be distinguished more readily in the free-flowing reaches than in the impounded reaches of the river.

Although the growth-at-age was not reported, the USGS measured weights and lengths fish they collected in 1998 and 1999. The results are shown in Table 13. The weights of the fish corresponded closely to their lengths. In general, the largest fish were caught in the Trentwood reach. Fish in this area benefit from better habitat conditions than fish in other reaches. Surface water in the Trentwood reach is more diluted with clean cool water than other reaches because significant in-flow of groundwater from the Spokane-Rathdrum aquifer occurs there. Other than the peak in average size at Trentwood, the trend in average weight and length of fish is greater as one proceeds downstream.

Table 13. Spokane River fish taxa, weights, and lengths, 1998 and 1999

<i>Post Falls, 1998</i>			
Species	# Caught	Avg. wt.	Avg. length
Largemouth bass	3	13	95
Largescale sucker	28	4	67
Northern pikeminnow	28	32	98
Redside shiner	29	8	88
Speckled dace	34	5	70
Torrent sculpin	2	7	82
Yellow bullhead	1	39	138
<i>Post Falls, 1999</i>			
Species	# Caught	Avg. wt.	Avg. Length
Black crappie	8	48	136
Brown bullhead	1	58	160
Largemouth bass	2	9	80
Largescale sucker	14	333	215
Northern pikeminnow	3	241	252
Pumpkinseed	8	14	77
Redside shiner	1	17	110
Smallmouth bass	1	87	175
Speckled dace	19	3	55
Yellow bullhead	1	7	68
Yellow perch	5	6	75

Trentwood, 1999

Species	# Caught	Avg. wt.	Avg. Length
Brown trout	1	311	303
Chinook salmon	1	816	480
Cutthroat trout	2	268	282
Largescale sucker	29	851	399
Longnose dace	5	4	59
Longnose sucker	1	600	360
Northern pikeminnow	1	324	315
Rainbow trout	17	521	337
Speckled dace	8	4	58

7 Mile Bridge, 1998

Species	# Caught	Avg. wt.	Avg. Length
Bridgelip sucker	48	861	424
Bridgelip sucker x Largescale sucker	3	817	420
Largescale sucker	43	661	354
Mountain whitefish	2	21	129
Northern pikeminnow	1	179	262
Rainbow trout	10	555	396
Redside shiner	2	19	113
Total	109	716	381

7 Mile Bridge, 1999

Species	# Caught	Avg. wt.	Avg. Length
Bridgelip sucker	65	288	232
Bridgelip sucker x Largescale sucker	5	776	406
Chiselmouth	3	9	79
Largescale sucker	23	719	384
Mountain whitefish	24	274	273
Northern pikeminnow	9	124	142
Rainbow trout	27	313	278
Redside shiner	6	5	65
Speckled dace	4	2	47
Torrent sculpin	3	12	61

Otis Orchards, 1999

Species	# Caught	Avg. wt.	Avg. Length
Black crappie	3	66	143
Largescale sucker	41	686	348
Longnose dace	20	3	58
Northern pikeminnow	4	533	378
Rainbow trout	14	535	336
Redside shiner	1	8	85
Smallmouth bass	1	144	195
Speckled dace	22	3	54
Torrent sculpin	1	17	98

Green Street, 1999

Species	# Caught	Avg. wt	Avg. Length
Black crappie	3	71	147
Largescale sucker	49	558	351
Longnose dace	1	8	86
Mountain whitefish	13	346	315
Northern pikeminnow	6	180	193
Rainbow trout	26	213	238
Rainbow trout x Cutthroat trout	1	279	302

The USGS examined these fish for several health condition indicators: deformities, eroded fins, lesions, tumors, anchor worms, Black Spot disease, leeches, parasitic skin fungi, *Ichthyophthirius* sp., and other external parasites, no-eyes, and Popeye disease. The number of fish with each of these indicators reported. The fish health indicator data are presented in Table 14, and graphically in Figure 15.

Table 14. Spokane River fish health indicator data, 1998 and 1999

Year	1998		1999				
	Post Falls	7 Mile	Post Falls	Otis Orchards	Trentwood	Green Street Bridge	7 Mile
RM	102	61.4	102	96	86	77.8	61.4
Fin Erosion	0	1/43 Largescale suckers	3/8 Black Crappie	1/3 Black Crappie; 1/40 Largescale suckers	0	3/49 Largescale suckers	1/5 Rainbow trout
Skin Lesions	0	11/43 Largescale suckers	0	3/40 Largescale suckers	0	1/49 Largescale suckers	1/22 Largescale suckers
Deformities	0	5/48 Bridgelip suckers	0	0	0	1/6 Northern Pikeminnows	0
Fungus	0	1/48 Bridgelip suckers	0	0	0	0	0

Figure 15. Fish health indicator data, Spokane River, 1998 and 1999

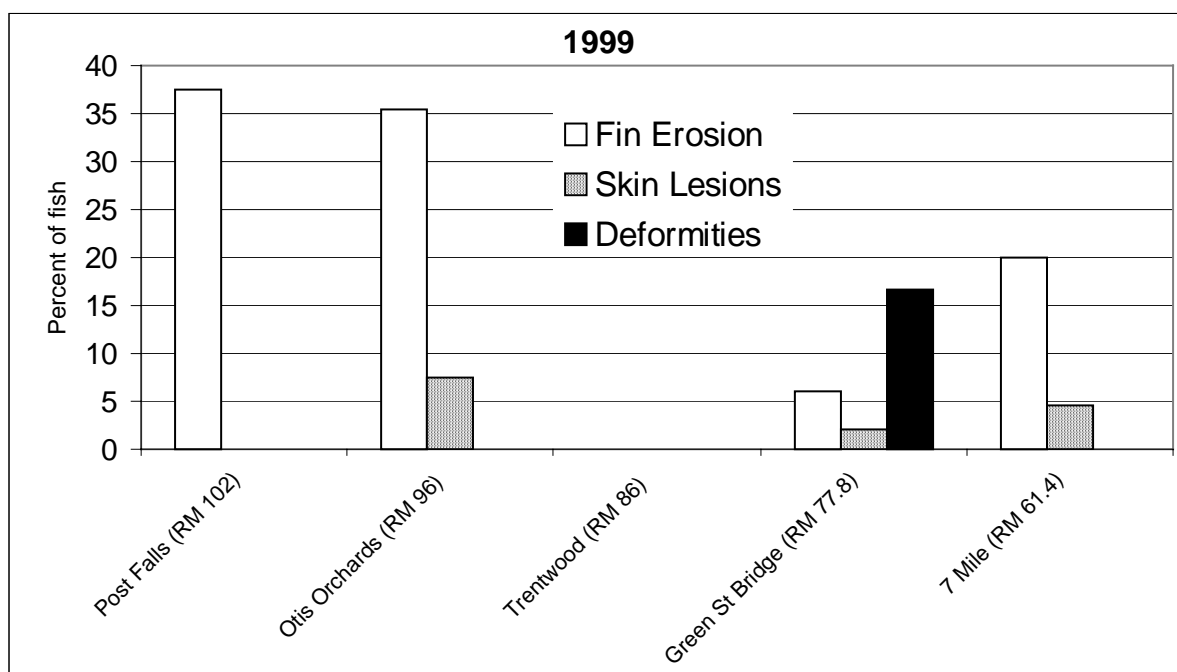
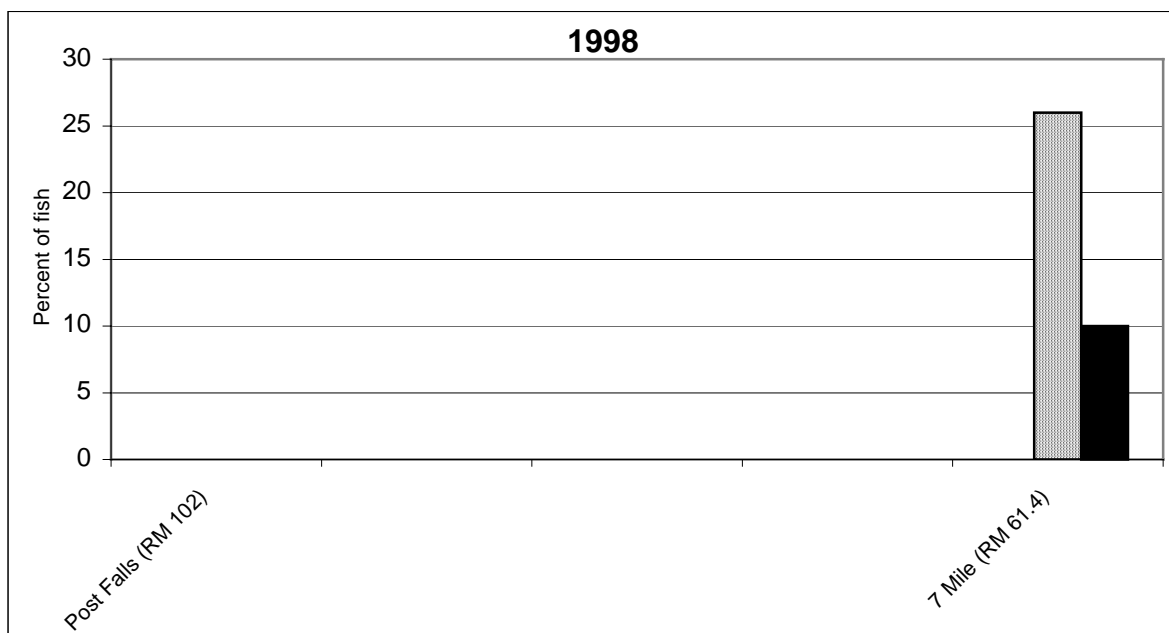


Figure 15. (continued)



None of the fish collected in either 1998 or 1999 at any site were reported to have any visible anomalies other than those included in Table 14 and Figure 15. In the more comprehensive 1999 collection, the incidence of fin erosion appears to decline progressing down stream; however, no fin erosion was reported in the 1998 samples, even at Post Falls (RM 102). In 1999, some fish collected at Green Street had deformities, but not at Seven Mile. The Rainbow trout collected at Seven Mile included fish that had been stocked. It is possible that the fin erosion seen in one of the five Rainbow trout collected there resulted from hatchery-related trauma, as opposed to environmental chemical stress.

Overall, no definite pattern in the incidence of fish health effects is evident. The high heterogeneity of the incidence of observed health impairments may be related to low survival of fish with greater degrees of impairment: such fish cannot survive long and thus do not make up a significant portion of the population, although many may be affected and die prematurely over time. A quantitative determination of the individual effect level (e.g. percent of body surface involved, internal pathological examination, etc.) might have clarified this possibility, but no such information was available. In addition, the low incidence of obvious health impairments does not preclude the possibility of significant incidence of less apparent sublethal effects, which could result from various mechanisms of metal toxicity, previously mentioned.

Piscivorous Bird Assessment

Piscivorous birds and other wildlife are exposed to Zn and other metals via water, soil, and food items. Among the terrestrial wildlife within the SR corridor, piscivorous birds are likely to be at greatest risk from excessive exposure to metals by these routes.

Zn in fish tissue exceeds the NOAEL-based wildlife benchmark for Osprey (72.5 mg/kg fish tissue) but is below the LOAEL-based benchmark (Sample et al. 1996). There is no evidence of biomagnification of Zn or other mining-related metals in the food web trophic levels below those of piscivorous birds, despite substantial metal bioaccumulation in the fish they eat. Thus, dietary exposure levels in such birds are probably near the same level as those for larger piscivorous fish; however, no data on tissue metals levels in any SR bird species are available to confirm this. The only available data on piscivorous birds in the SR corridor came from Payst (1994), who performed a two-year study on the nesting ecology of the Osprey (*Pandion haliaetus*) population within the corridor, from Lake CdA to Little Falls (below Long Lake). He observed this population to feed only on fish: Yellow perch (*Perca flavescens*), Yellow bullhead (*Ictalurus natalis*) and various salmonid species (primarily Rainbow trout). He concluded that nesting success was high and that the population is increasing in size. No other studies on piscivorous birds living in the SR corridor were found. This finding is consistent with the apparent lack of metal biomagnification at primary and secondary consumer trophic levels.

Despite the long awareness of metals exposure threats to wildlife in the SR corridor, no other data were available to assess effects of exposure to metals in SR wildlife. In addition to studies of wildlife populations, bioassays exposing bird species to SR media or food items should be considered.

Population Fitness

As subsequent generations of aquatic organisms are chronically exposed to toxic levels of environmental contaminants, their populations may develop resistance, as the progeny of surviving individuals outnumber less tolerant individuals, becoming more fit for their environment. The costs of this fitness may be a trade-off of reduced growth rates or fecundity for greater survival. Although Kleist (1987) found Rainbow trout growth-at-age to be nearly normal, he was only looking at fish from below the City of Spokane in the SR. Genotypic metal tolerance cannot be ruled out as a factor in the low spawning success reported by Bennett and Underwood (1988) and Johnson (1997).

Resistant populations may also have reduced genetic options for dealing with newly arising stresses (Walker et al. 1996). Genetic variability and structure are an important characteristic of contaminated ecosystems because of the positive correlation of genetic variation with fitness measures (Mitton and Grant, 1984), and increased potential for adaptability in non heterogeneous habitat (Nevo et al. 1986). If differing traits amongst individuals of a population allow them to respond differentially to stressors (e.g., metal pollution), a population with high trait diversity will have a better probability of having a resistant form than will a population having less diversity. Thus high initial trait diversity is likely to confer continued existence of a species at a contaminated site. On the other hand, if a certain stressor eliminates all individuals except those with a resistant genotype, the population will be left vulnerable to subsequent stressors, reducing long-term perpetuation. A study done by Roark and Brown (1996) provides evidence that contamination with Zn ($\approx 735\text{-ug/L}$) and Pb ($\approx 35\text{-ug/L}$) (at hardness $\approx 470\text{-mg/L}$) caused significant changes in genetic structure of fish populations in Soda Butte Creek, MT, relative to populations from reference sites. In the same way, less metal-tolerant forms may have been eliminated from populations in the SR.

No studies of genetic structure of populations of any SR species were found in the literature. However, it is very likely SR species have adapted genetically in the same way as have populations in other rivers that have similar metal contamination. In some of these studies, investigators have concluded that populations have lost degrees of adaptability to other stressors. SR resident species have long been exposed to- and have adapted to high levels of Cd, Pb, and especially Zn. Thus, it is probable that populations have lost some degree of their normal capacity to adapt to other stressors.

Data Summary

The apparent effect of exposure to metals and other stressors is summarized in the following tables. The most conservative of the water-column benchmarks is the Sensitive Species EC20, which is the highest concentration that could cause less than 20% reduction in growth, fecundity, or other sub-lethal endpoint in the most sensitive 5% of species tested. Stated differently, a Sensitive Species EC20 for a given metal is the concentration of that metal that would cause a 20% decrease in growth (or some other chronic endpoint) for the 5% of species known to be the most sensitive to that metal. Only freshwater species are used to calculate this benchmark. At their average annual concentrations, Cd and Zn exceed this benchmark to at least RM 64. The Sensitive Species EC20 for Pb is exceeded at the mean concentration to RM 96 and at the maximum concentration to RM 85.3. Based on this, risk for significant chronic effects is estimated for 5% of the aquatic species in much of the upper river.

Water Column Risk Summary

The observed water column metal concentrations are compared with various water quality benchmarks in Table 15. If the maximum or mean metal concentration exceeded a benchmark for that metal, the metal is listed in the table. Water column metal concentrations are compared to different benchmarks in order to discriminate risk levels to different taxa. For explanations of the benchmarks, see the previous section on Water Quality Criteria and Benchmarks.

Table 15. Comparison of dissolved metal concentrations¹ to Water Quality Criteria and other ecological benchmarks²

Benchmark	Metal Concentration > Benchmark					
	RM 96		RM 85.3		RM 64	
	Mean	Max	Mean	Max	Mean	Max
NAWQAC		Zn		Zn		
NAWQCC		Zn		Zn		
LCV Fish	Zn	Zn	Zn	Zn	Zn	Zn
LCV Daphnids	Cd, Zn	Cd, Zn	Cd, Zn	Cd, Zn	Zn	Cd, Zn
LCV Aquatic Plants	Zn	Zn	Zn	Zn	Zn	Zn
LCV All organisms	Cd, Zn	Cd, Zn	Cd, Zn	Cd, Zn	Zn	Cd, Zn
LT EC20 Fish	Zn	Zn	Zn	Zn	Zn	Zn
Sensitive Sp. Test EC20	Cd, Pb, Zn	Cd, Pb, Zn	Cd, Zn	Cd, Pb, Zn	Cd, Zn	Cd, Zn
Population EC25	Zn	Zn	Zn	Zn	Zn	Zn

Sources: ¹ Summary of Spokane River data from July, 28 1992 – Sept. 8 1993 (Pelletier 1994).

² Suter and Tsao, 1996.

The NAWQAC and NAWQCC for Zn were exceeded at least to Barker Road (RM 90.4) in May and September, 1999. Determinations were based on dissolved concentrations estimated from total concentrations from Roland (unpublished) adjusted for solubility based on the average dissolved-total proportions noted in the Bioavailability section, above. Making this adjustment provides a conservative estimate of exposure since NAWQAC and NAWQCC are derived from “total” measured metal concentrations in bioassays done in clean laboratory water that is low in particulates, which would sorb metals making them not bioavailable. Criteria may have been exceeded at other times during 1999. Concurrent hardness data for calculation of the criteria were provided only for May and September. These two sample sets were used for calculation of the criteria. Arsenic (As) and Cd data were not available either.

Sediment Risk Summary

Comparison of sediment metals concentrations to sediment benchmarks, bioassays of sediment samples, and macroinvertebrate community effects are presented in Table 16. The plus symbol (+) indicates that a concentration exceeds a benchmark or that an apparent effect is occurring in a location. Two plus symbols (++) indicates a greater exceedence or stronger apparent effect. A minus symbol (-) indicates no benchmark exceedence or apparent effect.

Table 16. Sediment risk summary and river reach scores

RM / I.D.	TEL				PEL				UET				Sed. Tox.	Benthos			Score
	As	Cd	Pb	Zn	As	Cd	Pb	Zn	As	Cd	Pb	Zn		Rich- ness	EPTC	% Dom. Fam.	
Post Falls 96 – 102	+	+	++	++	+	+	++	++	+	+	++	++		+	+	+	1
Otis Orchards 96 – 92														+	+	+	2
Greenacres 91 – 88														+	+	+	2
Trentwood 88 – 84														+	+	–	2
Upriver ~ 83	+	+	+	+	–	–	+	+	–	–	+	+	+				1
Upriver Dam ~ 81	+	+	+	++	–	+	+	++	–	+	+	++					1,3
Green Street ~ 77														+	+	–	2
7 Mile Bridge ~63	+	+	+	+	–	–	–	+	–	+	–	–		+	+	–	1
Nine Mile ~60	+	+	+	+	–	–	–	+	–	+	–	–					1
Long Lake ~52	+	+	+	+	–	+	+	+	–	+	–	+					1
“ ~49	+	+	+	++	–	–	+	+	–	+	+	+					1
“ ~39	+	+	+	+	–	–	–	+	–	+	–	–	+/-				1
Little Falls G-55	–	+	+	+	–	+	–	+	–	+	–	+					1
Spokane Arm G-33	–	–	+	+	–	+	–	+	–	–	–	+					1
G-23	–	+	+	+	–	+	+	+	–	+	+	+	+				1
G-28	–	+	+	+	–	+	+	+	–	+	+	+					1
Liberty Lake G-60	–	–	+	–	–	–	+	–	–	–	–	–					2
Hangman Cr.	–	–	+	–	–	–	–	–	–	–	–	–					4
Deep Creek	–	–	+	–	–	–	–	–	–	–	–	–					4
Little Spok. R. G-10	–	–	+	–	–	–	–	–	–	–	–	–					4

1. Evidence of metal-induced degradation
2. Metals may be stressing the system
3. PCBs are also at levels with potential to cause degradation
4. Little or no evidence of metal-induced degradation

Comparison of Horowitz's (in press) <2 mm size sediment fraction metal concentrations to TEL, PEL, and UET benchmarks indicates that benthic organisms are probably being adversely effected throughout the entire river, particularly in Long Lake and above. The limited benthic community assessment and bioassay data tend to support this conclusion. Adverse effects to benthic organisms were partially confirmed in the three locations that had both bioassay and metal analyses. Unfortunately, none of these locations also had benthic community assessment data. In locations where benthic communities were assessed, effects were most likely due to metals. Only one location where benthos were sampled (the Post Falls reach) also had metals data. No locations had both bioassay and benthic assessment data. Ideal sediment assessment designs have all three types of data from each sample location.

Risk Characterization

In the following sections, the relationships between available data for each of four major biotic communities of the SR are explored so that the risks of elevated metals exposure and other environmental factors are accounted.

Primary Productivity

Significant alteration to the SR phytoplankton community from Zn is apparent. For algae and other phytoplankton species, Zn exposure occurs almost exclusively through the water column. The year-round average water column Zn concentration exceeds the LCV-Plants at least to RM 64. Zn exposure is typically highest from December through April, and toxicity to periphyton and other plant species is expected to be most pronounced during this period. Cd and Pb may slightly contribute to toxicity at the levels at which they are present, as may many other contaminants originating from agricultural, industrial, and urban non-point and point sources along the river. In SR water bioassays using *Selenastrum capricornutum*, conducted in the 1970s and 1980s, strong growth algal inhibition could be reversed by addition of a metal chelating agent to the water. These studies supported the conclusion that metals were responsible for toxicity. The Zn levels in the bioassays fell between the current mean and maximum Zn concentration above RM 85. No recent laboratory bioassays exposing algal species to SR water have been reported. In studies conducted in the 1970s and 1980s, SR phytoplankton community assessments revealed an absence of metal intolerant phytoplankton species. The most recent assessment of primary production is consistent with continued impairment of this ecological function: Field studies, conducted by USGS in 1998 and 1999, measuring chlorophyll, pheophytin a, and ash-free dry weight, indicate primary productivity is very low for the river above the City of Spokane WWPT.

Taken together, there is substantial evidence to support the conclusion that high metals concentrations, particularly Zn, are suppressing primary productivity of the SR. Thus, Zn appears to cause a major ecological impact by affecting the entire phytoplankton community in sufficient magnitude to cause a decline in abundance and changes in distribution, beyond which natural recruitment (reproduction, immigration from unaffected areas) is not returning the affected populations to their natural levels.

Macroinvertebrate Community

Macroinvertebrates are at risk from Zn and other contaminants through water column and dietary exposure. In addition, direct exposure to contaminated sediment occurs for those species that spend some or all of their life cycle in sediment habitats.

The Zn LCV-Daphnids is a macroinvertebrate-specific water quality benchmark that has been exceeded at least to RM 63 at the average Zn water-column concentration. Average Cd concentrations exceed the Cd LCV-Daphnids to at least to RM 85, and at times when Cd concentrations are near the typical maximum, the Cd LCV-Daphnids is exceeded to at least RM 64. The LCV-Non-Daphnid-Invertebrates benchmark is >5243-ug/L. None of the reported water sample concentrations approach that level.

For many macroinvertebrate species, dietary exposure to metallic contaminants occurs through ingestion of periphyton, plankton, and organic detritus. This route of exposure likely plays a major role in overall metal bioaccumulation in the SR. Metal bioaccumulation has been confirmed in Caddisflies in the Washington reaches recently (USGS 1998,1999), and in other SR-dwelling species in the Idaho reach by Farag et al. (1994). Organisms in higher

trophic levels, such as fish, that consume various macroinvertebrates, are then exposed to the bioaccumulated metals by ingestion of contaminated prey items.

For sediment-dwelling macroinvertebrates, metal-caused adverse effect risks vary locationally. Comparisons of sediment metal concentrations with sediment quality benchmarks indicate adverse effects in sediment dwelling species are likely. In SR impoundments and parts of the Spokane Arm, Cd, Pb, and Zn concentrations exceed the least conservative of the three benchmarks cited in this report: the PEL, which represents the lower limit of the range of contaminant concentrations that are usually- or always associated with adverse biological effects. Zn and Cd also exceed PEL benchmarks in free-flowing, non-depositional reaches, with increasing magnitude proceeding upriver toward the sources of the metals in Idaho. Sediment toxicity to SR sediment-dwelling macroinvertebrates is probable throughout much of the river.

Evidence supporting the benchmark-based toxicity prediction comes from recent laboratory sediment bioassays using benthic invertebrates (Batts and Johnson 1995). In these tests, apparent toxicity corresponded to bulk metals concentrations in the tested samples. The bioassays, although very limited in geographic scope, suggest sediment metal contamination is severe enough to cause community level effects in sediment-dwelling macroinvertebrates, at least in some locations.

Certain physical environmental factors and the presence of other contaminants probably add to the adverse effects of high metals exposure. Dissolved oxygen normally fluctuates, and when levels increase in overlying river water, an increase in the bioavailable portion of sediment-associated metals is expected as acid volatile sulfides are oxidized and release bound metals. Declining pH in overlying waters is also expected to increase metal bioavailability in sediments. Increasing water temperatures generally increase bioaccumulation of metals, and thereby the risk of toxic effects. Among the non-metal chemical stressors, PCBs have been identified as contaminants of concern in the SR. For macroinvertebrates, exposure to PCBs occurs at very low levels via the water column and at higher levels from contact with sediment pore water, and by ingestion of contaminated food such as periphyton, plankton, and organic detritus. PCB bioaccumulation has resulted in elevated tissue concentrations in fish extending from above the Upriver Dam to the Spokane Arm (WDOE 1995; Golding 1996). Organic carbon normalized sediment PCB concentrations are highest behind the Upriver Dam (RM 80.6) and opposite Inland Metals (RM 75.4). Concentrations exceed the Ontario Severe Effects Level (as cited by Johnson et al. 1994), which is a guideline intended to indicate risk to benthic communities. In addition to PCBs, other contaminants from current and historic, urban, industrial, and agricultural point and non-point sources may add to the overall level of metal-induced toxicity to SR macroinvertebrates in the Spokane.

Recent assessments of riffle-dwelling macroinvertebrate communities at several sites in the SR showed lower abundance of such organisms in upstream areas, closer to the sources of metal contamination. The findings of decreased species richness and ratio of Ephemeroptera, Plecoptera, Trichoptera and Chironomidae abundance, and increased percent contribution of dominant taxa, in the river east of Spokane, indicate less healthy macroinvertebrate communities in areas of higher metals bioavailability and generally higher sediment metals concentrations. The most striking aspect of the macroinvertebrate surveys was the complete absence of Plecoptera (Stonefly) species. Plecoptera tend to be relatively pollution intolerant compared to most macroinvertebrate species. Their total absence in recent surveys indicates a severe impact to macroinvertebrate community structure.

Taking together all available information on the SR macroinvertebrates, population-level effects appear to be severe. Entire populations of sensitive species are affected in sufficient magnitude to cause a change in distribution beyond which natural recruitment has not returned the populations to their natural levels. The ecological significance of this damage is a reduction in productivity, which is likely causing undesirable effects on valued species (game fish) because such species depend on abundant and diverse macroinvertebrate populations as food. However, it is unknown to what extent ecological parameters, such as predator-prey relationships, are also subsequently affected by this imbalance. In addition, macroinvertebrates are also involved in nutrient cycling (Wallace and Webster, 1996) and reduction of their populations may worsen nutrient-related water quality problems.

Fish Community

Fish are at risk from Zn and other contaminants through the water column and dietary exposure. In addition, some fish species are exposed to contaminated sediment directly.

In addition to National Ambient Water Quality Criteria, fish-specific water quality benchmarks have also been exceeded recently and in the past. The average Zn concentration exceeded the LCV-Fish, the LT-EC20-Fish, and the Population EC25 at least to RM 63 during 1992-1993. The Zn concentration exceeded the LCV-Fish to at least RM 90 from 12/1998 to 8/1999; to at least RM 75 from 12/1998 to 7/1999 and; to at least RM 39 from 1/1998 (or earlier) to at least 4/1999. These data indicate that Zn concentrations are at levels chronically toxic to one or more fish species, as reported in scientific literature.

Exceedence of other benchmarks, at least to the City of Spokane (RM 75), were noted. The water-column Zn concentration exceeded the LT-EC20 Fish from 12/1998 through at least 6/1999, and Population EC25 from 12/1998 through at least 4/1999. Exceedence of the test EC20 for fish, suggests Zn concentrations may be causing significant reduction in weight (and thereby probably the survival) of young fish. Exceedence of the Zn Population EC25 suggests that from January through April, from Post Falls to Harvard Road, population-level effects are likely. In other words, Zn concentrations are above those that would cause a 25% reduction in the abundance of largemouth bass, which is a centrarchid species that is typically less sensitive to metals than the salmonid species of concern in the SR. No fish specific benchmarks for Cd were exceeded in the 1992-1993 data. Cd concentration data for 1998 or 1999 were not evaluated during this assessment. No fish specific Pb benchmarks were exceeded in the 1992-1993 or 1998-1999 data.

Exceedence of fish-specific Zn benchmarks indicates risks of adverse effects in individuals and populations of some species. No effort to gather laboratory evidence supporting or refuting the prediction of toxicity has been made recently. No SR bioassay using fish have been reported since 1982. Bailey and Saltes (1982) reported that SR water was not overtly toxic to wild caught SR Rainbow trout. Earlier still, Funk et al. (1975) reported that fish in the SR were surviving in concentrations of Zn approximately five times the amount found to be the median lethal concentration (90 ug/L) in laboratory studies. Unacclimated Rainbow trout were killed by short exposures to SR the same water. Bailey and Saltes (1982) researched the factors contributing to the existence of what they described as a healthy salmonid population in the SR, which contained Zn concentrations of approximately 100-ug/L, at the time. Their results indicated that SR Rainbow trout could tolerate more than 10 times as much Zn, Cd, and Pb as unacclimated trout. Hatchery trout that were acclimated to 100 ug/L had higher tolerance to SR water but were far more susceptible than indigenous SR trout.

The high metals tolerance of SR Rainbow trout compared to unacclimated trout indicates profound metal adaptation by the SR population. Other river-dwelling species, chronically exposed to high metals concentrations for the past century, have likely been selected for metals tolerance as well. Thus, acclimation may counter community level effects in fish to some degree. This is expected because, as subsequent generations of aquatic organisms are chronically exposed to toxic levels of environmental contaminants, they may develop resistance and become more fit for their environment. Unfortunately, the costs of such fitness may be a trade-off of growth rate or fecundity for greater survival. Fish with reduced growth rate, or impaired health, could be eliminated from natural populations where metal stresses are present. This theory is supported by Bennett and Underwood's (1998) study of SR fish recruitment. They assessed Rainbow trout abundance, mortality rates, seasonal distribution, movement, spawning and rearing habitat, and recruitment for the Idaho reach of the SR. Their work indicated the population suffered high mortality (70%, with only 10% attributed to fishing). They suggested recruitment was insufficient and that high metals concentrations were the probable cause, either alone or in combination with other likely causes, i.e., low stream flow and high temperatures ($>23^{\circ}\text{C}$).

The ecosystem attribute of greatest concern is perhaps the fishery, but recent fisheries assessment studies are without suitable reference sites. Because the river has been stocked with game fish many times, and is dammed in four places, there is no direct way to assess impairment to the SR's native fish populations. Community structure analyses of the fishery could be performed only on a limited basis. In addition, little data on comparable rivers is available. This lack of information precludes convenient examination of the ecological status of the fishery.

The USGS collected fish in several locations on the SR in 1998 and 1999. The species composition in these collections was heterogeneous. The data suggests improvement in intolerant fish species abundance progressing downstream, at least in free flowing reaches. Overall, no definite pattern in individual fish health indicators was evident in the 1998 and 1999 USGS fish collections. However, the high heterogeneity of observed health impairments may have been related to low survival of fish with greater degrees of impairment. Fish population data are inconclusive – there is little direct evidence of impairment. In addition to metals, other conditions (primarily poor habitat, low flow, and excessive temperature) are likely affecting salmonid populations. Significant adverse effects in fish and other aquatic organisms populations are expected because of the aggregate risk of the combination of Cd, Pb, Zn and other pollutants.

Dietary exposure to metallic contaminants in fish occurs through ingestion of contaminated fish, macroinvertebrates, periphyton, plankton, and other food items. The type of food consumed depends on the niche occupied by the species, and is determined in part by the size and age of the fish. Dietary exposure likely plays a major role in metal bioaccumulation for all SR River fish. Metal bioaccumulation has been confirmed in Rainbow trout and Largescale suckers in the Washington reaches of the river in 1998-1999 (USGS 2000) and in Mountain whitefish in 1999 (Johnson 2000). Based on laboratory studies, adverse effects in fish embryos or juveniles are expected to correspond to the tissue levels observed. Toxicity tests on water from the upper CFR, which is similar in metals contamination to the SR, have demonstrated that fish health is adversely affected following exposure to water and diet at these levels of contamination.

For sediment-associated fish species, such as sculpins and suckers, metal-induced adverse effect risks vary based on location. Upriver depositional areas pose the greatest risk, whereas river reaches, where deposition or settling of contaminated solids is least, pose the least risk.

Physicochemical environmental factors and the presence of other contaminants probably add to the adverse effects of high Zn exposure in fish. As noted previously, Zn exposure is typically highest from December through April, and toxicity to fish is expected to be most pronounced during that period. Cd and Pb may slightly contribute to fish toxicity. Increasing water temperatures generally increase bioaccumulation of metals and therefore the risk of toxic effects. Thus, elevated summer water temperature probably enhances the toxicity of Zn and other contaminants to fish. An increase in dissolved oxygen levels in overlying river water is expected to increase the bioavailable portion of sediment-associated metals as acid volatile sulfides are oxidized and release bound metals. Declining pH in overlying waters is also expected to increase metal bioavailability in sediments.

Among the risks from other contaminants, exposure to PCBs occurs at low levels via the water column, at higher levels from contact with sediment pore water, and by ingestion of contaminated food. Fish tissue PCB levels are highest in populations living in, or associated with the Upriver Dam impoundment. In addition to PCBs, other contaminants common to current and historic urban, industrial, and agricultural point and non-point source pollution along the river are likely to add to the overall level of metal induced toxicity to fish in the Spokane.

Considering all available information, there is evidence of metal-induced degradation to the fishery, but the severity of the impact can not be determined using existing information. Community level effects in SR fish have probably occurred, and are still occurring, because of elevated Zn and other factors. The ecological significance of damage to these communities is a reduction in sensitive fish species populations and increased populations of tolerant fish species: an upset in the balance of the fish community structure. However, it is unknown to what extent ecological parameters, such as predator-prey relationships, are subsequently affected by this imbalance. The weight of evidence from fishery studies indicates the fish community, to at least RM 75, is at risk from metal contamination. In addition, poor habitat, high temperatures, low productivity (limited food), PCBs, and probably other contaminants may be interacting to impair fish productivity.

Piscivorous Birds

Piscivorous birds and other wildlife are exposed to Zn and other metals via water, soil, and food items to various degrees. Among the terrestrial wildlife within the SR corridor, piscivorous birds are likely to be at greatest risk from excessive exposure to metals by these routes. Zn in fish tissue exceeds the NOAEL-based wildlife benchmark for Osprey (72.5 mg/kg fish tissue) but is below the LOAEL-based benchmark (Sample et al. 1996). There is no evidence of biomagnification of Zn or other mining-related metals in the food web trophic levels below those of piscivorous birds, despite substantial metal bioaccumulation in the fish they eat. Thus, dietary exposure levels in such birds are probably near the same level as those for larger piscivorous fish; however, no data on blood or other tissue metals levels in any SR bird species are available to confirm this. Similarly, no bioassays exposing any bird species to SR media or food items have been conducted.

Other chemicals from effluent point sources and runoff non-point sources along the Spokane also contribute to the aggregate ecological stress within the river. PCBs are

contaminants of potential ecological concern in the SR. Fish tissue PCB levels exceed various guidelines for protection of piscivorous wildlife (as cited in WDOE 1995). The level of PCBs in fish tissue greatly exceeds the NOAEL-based wildlife benchmark for Osprey (0.014 ug/g, fish tissue) but is below the LOAEL-based benchmark (Sample et al. 1996). Total PCB levels also exceed the guideline of Newell et al. (1987) for protection of piscivorous wildlife (0.11 ug/g wet wt. fish tissue).

However, no direct evidence is available to confirm or refute effects. A single 2-year field study on nesting success (Payst 1994) shows that the SR Osprey population from Lake CdA to Little Falls is healthy. However, this study was not designed to test for population effects from pollutants. An appropriately designed study would be needed for sufficient confidence in the conclusion of no effects. Nonetheless, Osprey are piscivorous, and therefore Payst's observance of Osprey nesting success is, at least indirectly, consistent with the apparent lack of metal biomagnification to upper food web consumer trophic levels.

Conclusions

Contamination of SR water, sediment, and biota by Cd, Pb, Zn and other metals of CdA mining district origin appears to have declined since the 1970s, but remains at concentrations of environmental concern. The metals observed in these media are still at levels well above normal background concentrations. In addition to long-term trends, there are short-term annual variations in water column metal exposures, which depend largely on flow (time of year). Exposure risks also depends on position within the river.

Recent monitoring has shown that Cd, Pb, and Zn exceed NAWQCC at times, particularly in the river above the City of Spokane. These violations of federal water quality standards indicate that serious ecological harm is probably occurring from these metals. The concentration of Zn in much of SR exceeded the NAWCCC for significant periods of 1992 and 1993. Apparently, the chronic water quality criterion for Zn is approached or exceeded from Post Falls, ID at least to RM 85.3, which is in Washington, from December to April annually. Even the NAWQAC for Zn was exceeded above RM 90 during May 1999. It is likely this acute criterion was exceeded during the entire high flow period of the year, but data were available only for May and September of that year. The Cd NAWCCC was occasionally exceeded during 1992-1993 as well. More recent Cd monitoring data were not evaluated in this assessment. Pb NAWQCC were exceeded at least to RM 90 in May 1999, and at Post Falls (RM 101) in September 1999.

The Sensitive Species Test EC20s, which are conservative water quality benchmarks, are exceed by average Zn and Cd concentrations in SR water to at least RM 64. Average water Pb concentrations exceed SS-Test-EC20 to at least RM 96. When Pb concentrations are highest during spring flows, the Pb SS-Test-EC20 is exceeded to at least RM 85.3. This suggests that at least five percent of the aquatic species are at sufficient risk to result in reduction of their populations from metal contamination originating from the "Silver Valley" mining districts of northern Idaho.

The risk level for sediment exposure is determined mostly by location and by pH and dissolved oxygen in the overlying water. The Zn PEL and the Cd UET sediment quality benchmarks were exceeded at Post Falls (RM 100) and Seven Mile (RM 61.4) in samples collected in 1998. This indicates that sediment-associated species are likely suffering adverse effects down river to at least RM 64. The other data indicate that sediment-

associated species are likely suffering adverse effects throughout the river including the Spokane Arm.

Exceedence of water and sediment benchmarks trigger concern, but do not, by themselves, prove impacts have occurred. However, other evidence from the SR confirms clear impacts to phytoplankton and macroinvertebrate communities. Adverse effects observed in the toxicity studies suggest significant ecological impacts. Populations of primary producers, such as some species of plankton, have been greatly reduced from the state line and above, down at least to Long Lake. The reductions have been clearly linked to excessive Zn levels.

Populations of some macroinvertebrate species have been reduced or eliminated as far down river as the City of Spokane. Sediment bioassays and chemical analyses are consistent with the conclusion that metals are responsible for population effects in the exposed species. Levels of metals in the water exceed fish-specific criteria. Fish tissue metal levels suggest exposure is high enough to adversely affect fish populations. Bioassays with SR Rainbow trout indicate the fish population is highly tolerant to metals levels what would be acutely lethal to naïve Rainbow trout. Although the recent fish community data are somewhat equivocal, fish populations do appear to be suffering, and the degree of population impairment is proportional to proximity to sources of contamination in Idaho, even within the Washington portion of the SR.

Examination of food chain metals transfer suggests a slight risk from Cd and Zn. The bioassessment studies and food chain analysis suggested a lack of overt acute toxic effects. Indirect evidence suggests metal contaminated invertebrates may be responsible for sublethal responses affecting the health of SR fish. The effects are probably in the minor to moderate range. For fish, food chain transfer risk is likely at least down to RM 71, where Latah Creek enters. Trophic transfer of the Zn in fish to piscivorous wildlife may pose significant risks, especially in combination with PCBs, and other the toxicants that are present. Other species of wildlife may be at risk through trophic transfer of these contaminants, but no data have been collected with which assessments can be made.

A variety of sublethal effects are likely to be occurring in SR aquatic species. Lipid peroxidation and ionoregulatory imbalance cause energy to be diverted from growth to the maintenance of physiological homeostasis (Farag et al. 1994), even at low levels of metals exposure. Responses to low exposure levels are subtler and are less easily discernible than for higher exposure levels. However, in summation over the life cycle, such subtle responses are likely to be ecologically important at the population level (Forbes and Calow, 1996). There is not enough information available to assess firmly the risk of metals in this context for any SR aquatic communities other than phytoplankton and macroinvertebrates, for which impacts have been clearly demonstrated. Despite the lack of sufficient investigation of the other communities in the SR, the excessive levels of Zn and other contaminants pose a risk of toxic effects. This risk cannot be overlooked for these unstudied groups, especially when one considers the aggregate effect of all the contaminants together.

Much of the data on metals concentrations in the river, water, sediments, and tissues are over ten years old, adding to the uncertainty of the assessment. However, considering the older information along with more recently available data on SR water and sediment quality data, as well as SR biological data, the preponderance of information indicates metal-induced degradation ranging from major to minor in severity. Major ecological impacts in the SR are related to high metals concentrations, which are suppressing productivity in

phytoplankton and macroinvertebrate communities and probably other portions of the ecosystem. Entire populations are affected in sufficient magnitude to cause declines in abundance and changes in distribution beyond which natural recruitment is not returning populations to natural levels. This is true for all the river reaches that have been studied, and is most pronounced in the upper river phytoplankton (at least to Long Lake) and macroinvertebrate communities (down to at least Seven Mile).

In addition to phytoplankton and macroinvertebrate communities, fish communities in some reaches of the SR have been studied, as well. High exposure to Zn and other CdA mining district-related metals is likely affecting some fish species populations and probably has changed their abundance and distribution over many generations. However, the levels of effects do not appear to be threatening the continued survival of the studied populations.

SR wildlife populations have received almost no study, despite apparent risk from exposure to Zn and other contaminants at levels exceeding criteria for protection of wildlife. One study of SR Osprey provided indirect evidence suggesting that if adverse effects have occurred, they have had negligible to minor impacts. Minor impacts could be effects in a specific group(s) of localized individuals within a population over short periods, without effects on other trophic levels or populations. Additional empirical data would be necessary to confirm or refute this conclusion.

Integration of the results of the ecological studies with the effects observed in the bioassays indicates that the aquatic ecosystem above RM 71 shows at least moderate adverse ecological effects depending on the community studied, mostly caused by excessive Zn. Other chemicals or conditions exist with potential to cause degradation. Secondary ecological effects may be occurring in populations or species dependent upon metals-sensitive populations that have suffered declines in abundance and/or changes in distribution.

References

- Ankley, G. T., D. M. Di Toro, D. J. Hansen, and W. J. Berry. 1996. Technical basis and proposal for deriving sediment quality criteria for metals. *Environ. Toxicol. Chem.* 15(12):2056–2066
- Bailey, C. and L. Singleton. 1984. Spokane Industrial Park receiving water survey. WDOE. May.
- Bailey, G.C. and J. Saltes. 1982 a. Fishery assessment of the upper Spokane River. Report 46 WSU; UW; Wa Water Research Center. June.
- Bailey, G.C. and J. Saltes. 1982 b. The development of some metal criteria for the protection of Spokane River Rainbow trout. WSU. WDOE. December.
- Bartell, S.M. 1990. Ecosystem context for estimating stress-induced reductions in fish populations, pp. 167–182, in American Fisheries Society Special Symposium 8. Bethesda, MD.
- Batts, D. and A. Johnson. 1995. Bioassays of the Spokane River sediments. Memo to C. Nuechterlein and P. Hallinan, through L. Goldstien. February 27.
- Beattie, J.H. and D. Pascoe. 1978. *J. Fish. Biol.* 13:631-637.
- Bennett, D.H. and T.J. Underwood, 1988. Population Dynamics and Factors Affecting Rainbow Trout (*Salmo gairdneri*) in the Spokane River, Idaho. Completion Report No. 3. The Washington Water Power Company. February.
- Bortleson, G.C., S.F. Cox, M.D. Munn, R.J. Schumaker, E.K. Block, L.R. Bucy, and S.B. Cornelius. 1994. Sediment-quality assessment of Franklin D. Roosevelt Lake and the upstream reach of the Columbia River, Washington, 1992. USGS; USEPA. Open-file Report 94-315. USGS; WSU; USEWS; USEPA. October
- Brumbaugh, W.G. and J.W. Arms. 1996. Quality control considerations for the determination of acid-volatile sulfide and simultaneously extracted metals in sediments, Short Communication. *Environ. Toxicol. Chem.*, 15(3): 282-285
- Buchman, M.F. 1999. NOAA Screening Quick Reference Tables, NOAA HAZMAT Report 99-1, Seattle, WA, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration.
- Cairns, J., A.G. Heath, and B.C. Parker. 1975. The effects of temperature upon the toxicity of chemicals to aquatic organisms. *Hydrobiologia*, 47:135
- Carlson, A. R., G. L. Phipps, V. R. Mattson, P.A. Kosian and A.M. Cotter. 1991. The role of acid-volatile sulfide in determining cadmium bioavailability and toxicity in freshwater sediments. *Environ. Toxicol. Chem.* 10:1309-1319
- Crawford, J.K., and S.N Luoma. 1993. Guidelines for the studies of contaminants in biological tissue for the National Water-Quality Assessment Program: U.S. Geological Survey, Open File Report 92-494, 69 p.
- Cummins, J.M.; C.E. Gangmark, R.L. Arp, P.R. Davis, and S. Filip. 1981. An assessment of algal productivity in Spokane River waters collected from Lake Coeur d'Alene to Post Falls. March.
- Davies, P.H., W.C. Gorman, C.A. Carlson, and S.F. Brinkman. 1993. Effect of hardness on bioavailability and toxicity of cadmium to Rainbow trout. *Chem. Spec. Bioavail.* 5(2):67-77

- Di Toro, J.D. Mahhony, D.J. Hansen, J.K. Scott, M.B. Hicks, S.M. Mayro and M.S. Redman. 1991. Toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environ. Toxicol. Chem.* 9:1487-1502.
- Dixon, D.G. and J.B. Sprague. 1981. *Fish Biol.* 18: 579-589
- Eisler, R. 1974. Cadmium poisoning in *Fundulus heteroclitus* (Pices: Cyprinodontidae) and other marine organisms, *J. Fish. Res. Board Can.*, 28, 1225
- Eisler, R. 1988. Cadmium Hazards to Fish Wildlife and Invertebrates: A synoptic Review. USFWS Biological Report 85(1, 2).
- Ellis, M.M., 1940, Pollution of the Coeur d'Alene River and adjacent waters by mine wastes: Washington D.C., U.S. Bureau of Fisheries Special Report no.1.
- Falter, M.C. and B.D. Mitchell. 1982. Aquatic ecology of the Spokane River between Coeur d'Alene and Post Falls Idaho, 1980. Idaho Dept. Health and Welfare, Boise, ID.
- Farag, A.L., D.F. Woodward, E.E. Little, B. Steadman and L.A. Vertucci. 1993. The effects of low pH and elevated aluminum on Yellowstone cutthroat trout (*Oncorhynchus Clarki* Bouvieri). *Environ. Toxicol. Chem.* 12:719-731.
- Farag, A.M., C.J. Boese, D.F. Woodward and H.L. Bergman. 1994. Physiological changes and tissue metal accumulation in rainbow trout exposed to foodborne and waterborne metals. *Environ. Toxicol. Chem.* 13:2021-2024.
- Farag, A.M., D.F. Woodward, J.N. Goldstein, W. Brumbaugh, and J.S. Meyer. 1998. Concentrations of metals associated with mining waste in sediments, biofilm, benthic macroinvertebrates, and fish from the Coeur d'Alene River Basin, Idaho: Arch. *Environ. Contam. Toxicol.* 34:19-127.
- Ferrington, L.C. 1987. Collection and identification of floating exuviae of Chironomidae of use in studies of surface water quality. SOP No. FW 130A. U.S. EPA, Region VII, Kansas City, Kansas.
- Food and Agriculture Organization (FAO) of the U.N. 1980. Water quality criteria for European freshwater fish. Report on combined effects on freshwater fish and other aquatic life of mixtures of toxicants in water European Inland Fisheries Advisory Commission (EIFAC). Technical paper no. 37.
- Forbes, V.E. and P. Calow. 1996. Costs of living with contaminants: Implications for assessing low-level exposures. *Biological Effects of Low Level Exposures Newsletter.* 4(3)
- Funk, W.H., F.W. Rabe, and R. Filby. 1973. The biological impact of combined metallic and organic pollution in the Coeur d'Alene - Spokane River Drainage System. Project Completion Report: Washington Water Research Center. WSU. June.
- Funk, W.H., F.W. Rabe, R. Filby, G. Bailey, P. Bennett, K. Shah, J.C. Sheppard, N. Savage, S.B. Bauer, A. Bourg, G. Bannon, G. Edwards, D. Anderson, P. Sims, J. Rothert, and A. Seamster. 1975. An integrated study of the impact of metallic trace element pollution in the Coeur d'Alene - Spokane Rivers - lake drainage system. August.
- Funk, W.H., H.L. Gibbons, R.M. Duffner, T. Notestine, and T. Nielsen. 1983. Water quality of the upper Spokane River and evaluation of methods for measurement of the effect of effluent upon primary and secondary producers. WSU; UW; WA Water Research Center. Report 48. January.
- Gibbons, H.L., W.H. Funk, R.M. Duffner, T.S. Nielsen, and T. Notestine. 1984. Baseline study to determine the water quality and the primary and secondary producers of the Spokane River, Phase I. WSU; UW; WA Water Research Center. Report 57; -January.

Golding, S. 1996. Spokane River PCB source monitoring follow-up study November and December 1995. WDOE Pub. No. 96-331. July.

Greene, J.C., W.F. Miller, T. Shiroyama, R.A. Soltero, and K. Putnam. 1978. Use of laboratory cultures of *Selenastrum*, *Anabaena* and the indigenous isolate *Sphaerocystis* to predict effects of nutrient and zinc interactions upon phytoplankton growth in Long Lake, Washington (proceedings from the Symposium entitled Experimental Use of Algal Cultures in Limnology). International Association of Theoretical and Applied Limnology.

Halliwell, B. and J.M.C. Gutteridge, eds. 1985. *Free Radicals in Biology and Medicine*. Clarendon Press, Oxford, UK, pp. 139-170.

Hamilton, S.J., P.M. Mehrle, and J.R. Jones. 1987. *Trans. Am. Fish. Soc.* 116(4):541-550

Hassan, S.M., A.W. Garrison, H.E. Allen, D.M. Di Toro and G.T. Ankley. 1996. Estimation of partition coefficients for five trace metals in sandy sediments and application to sediment quality criteria. *Environ. Toxicol. Chem.* 15(12):2198-2208

Hattum, B. van, K.R. Timmerman, and H.A. Govers. 1991. Abiotic and biotic factors influencing in situ trace element levels in macroinvertebrates in freshwater ecosystems: *Environ. Toxicol. Chem.* 10:275-292.

Heath, A.C., 1987. *Water Pollution and Fish Physiology*, CRC Press, Boca Raton, FL,

Hodson, P.V. and J.B. Sprague. 1975. Temperature-induced changes in acute toxicity of Zn to Atlantic salmon (*Salmo salar*), *J. Fish. Res. Board Can.*, 32, 1

Hogan, J.W., and J.L. Brauhn. 1975. *The Progressive Fish Culturist* 37 (4):229-230

Holcombe, G.W., D.A. Benoit, and E.N. Leonard. 1976. *Trans. Amer. Fish. Soc.* 108:76-87

Homberger, M.I., J.H. Lambing, S.N. Luoma, and E.V. Axtmann. 1997. Spatial and temporal trends of trace metals in surface water, bed sediment, and biota of the upper Clark Fork Basin, Montana: U.S. Geological Survey, Open-File Report 97-669, Menlo Park.

Hopkins, B. and A. Johnson. 1997. Metal concentrations in the Spokane River during Spring 1997, Memorandum to Jay Manning and Carl Nuechterlein. Waterbody Numbers WA-54-1010, WA-54-1020, WA-57-1010. Washington Department of Ecology, Environmental Investigations and Laboratory Services. August.

Horowitz, A. 2000. *in press*.

Hoyle-Dodson, C. 1992. Water quality analytical data from Spokane Industrial Park. WDOE.

Ikramuddin, M. 1997. The use of lead 207/206 isotope ratios as an indicator of the source of lead in surface and ground water. Inland Northwest Water Resources Conference. An abstract presented at the Inland Northwest Water Resources Conference. April.

Ikramuddin, M., S. Box, and A.A. Bookstrom. 1997. Lead 207/206 ratios in sediments from the Coeur d'Alene and Spokane Area, Idaho and Washington, USA: Effect of mining activities on lead isotopic composition of sediments. EWU; USGS. May 25-29.

Ikramuddin, M. 1996. Use of Lead Isotopes to Identify the Source of Lead Contamination in Rivers, Lakes and Groundwaters. EWU. Geological Society of America Abstracts with Programs, v.28, p. A-215.

Ingersoll, C.G., W.G. Brumbaugh, F.J. Dwyer and N.E. Kemble. 1994. Bioaccumulation of metals by *Hyalella azteca* exposed to contaminated sediments from the upper Clark Fork River, Montana. *Environ. Toxicol. Chem.* 13:2013–2020.

Johnson, A. 1991. Review of metals, bioassays, and macroinvertebrate data from Lake Roosevelt benthic samples collected in 1989. WDOE. Memo from Art Johnson to Carl Nuechterlein. December.

Johnson, A. 1994. PCB and lead results for 1994 Spokane River fish samples. Memo from Art Johnson, WDOE, to Glen Patrick, WDOH. November.

Johnson, A. 2000. Results from analyzing metals in 1999 Spokane River fish and Crayfish samples. Memo to John Roland. WDOE. February.

Johnson, A., D. Serdar, and D. Davis. 1994. Results of 1993 screening survey on PCBs and metals in the Spokane River. WDOE. April.

Johnson, A.; D. Norton, B. Yake, and S. Twiss. 1990. Transboundary Metal Pollution of the Columbia River (Franklin D. Roosevelt Lake). *Environmental Contaminant Toxicology*; WDOE. 45:703-710.

Johnson, E. 1997. Upper Spokane River Rainbow trout spawning and emergence study for 1995 and 1996. Prepared for the Spokane River Management Team. November.

Kleist, T. 1987. An evaluation of the fisheries potential of the lower Spokane River: Monroe Street Dam to Nine Mile Falls Dam. Washington Water Power Company and Washington State Department of Wildlife. September.

LaPoint, T.W., S.M. Melancon and M.K. Morris. 1984. Relationships among observed metal concentrations, criteria, and benthic community structural responses in 15 streams. *J. Water Pollut. Control Fed.* 56:1030-1038.

Lauren, D.J. and D.G. McDonald. 1985. Effects of copper on branchial ionoregulation in the rainbow trout, *Salmo gairdneri* Richardson. *J Comp. Physiol. B* 155:635-644.

Leonhard, S.L., S.G. Lawrence, M.K. Friesen, and J.F. Flannagan. 1980. evaluation of the acute toxicity of the heavy metal cadmium to nymphs of the burrowing Mayfly, *Hexagenia rigida*. In: J.F. Flannagan and K.E. Marshall (Eds.), *Advances in Ephemeroptera Biology*. Plenum Publ. Corp. 157-465

Long, E.R., D.D. MacDonald, S.L. Smith, and F.D. Calder 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19(1), 81–97.

MacDonald, D.D. 1994. Approach to the Assessment of Sediment Quality in Florida Coastal Waters, Florida Department of Environmental Protection, Tallahassee, Florida.

MacLean, R.S., U. Borgmann, and D.G. Dixon. 1996. Bioaccumulation kinetics and toxicity of lead in *Hyalella azteca* (Crustacea, Amphipoda). *Can. J. Fish. Aquat. Sci.* 53(10):2212-2220.

Maret, T.R., and D.M. Dutton. 1999, Summary of information on synthetic organic compounds and trace elements in tissue of aquatic biota, Clark Fork-Pend Oreille and Spokane River Basins, Montana, Idaho, and Washington, 1974-96, U.S. Geological Survey Water-Resources investigation Report 98-4254.

Marking, L.L. and V.K. Dawson. 1975. Method for assessment of toxicity or efficacy of mixtures of chemicals. U.S. *Fish Wildlife Serv. Invest. Fish Control* 67:1-8.

- Matuszak, D.C., F.T. Downs, M.V. Schuler, and M. Ikramuddin. 1996. Impact of mining activities on the trace element geochemistry of the Spokane River, Idaho and Washington. EWU. Geological Society of America Abstracts with Programs, v.28, p. A-97.
- McGeachy, S.M. and D.C. Dixon. 1990. Effect of temperature on the chronic toxicity of arsenate to Rainbow trout (*Oncorhynchus mykiss*), *Can. J. Fish. Aquat. Sci.*, 47, 2228
- Miller, W.E., J.C. Greene, T. Shiroyama, E. Merwin. 1973. Use of Algal Assays to Determine Effects of Waste Discharges in the Spokane River System (proceedings from Biostimulation - Nutrient Assessment Workshop). USEPA, Eutrophication and Lake Restoration Branch, Pacific Northwest Environmental Research Laboratory. Program Element 1BA031. October.
- Mitton, J.B. and M.C. Grant. 1984. Associations among protein heterozygosity, growth rate, and developmental homeostasis. *Annu. Rev. Ecol. Syst.* 15:479-499.
- Moore, B.C., A. Thornburg, J. Schaumlöffel, R. Filby. 1996. Chironomid deformity rates, metal body burdens, and sediment metal concentrations from the Coeur d'Alene/Spokane River Systems. WA Water Research Center; USDOI. June
- Moore, J.N., S.N. Luoma, and D. Peters. 1991. Downstream effects of mine effluent on an intermontane riparian system: *Canadian Journal of Fisheries and Aquatic Sciences*, v.48, p.223-232.
- Mount, D.I. 1966. The effect of total hardness and pH on acute toxicity of zinc to fish. *Int. J. Air Water Pollut.* 10:49-56.
- Nevo, E. R., B. Noy, B. Lavie, A. Beiles and S. Muchtar. 1986. Genetic diversity and resistance to marine pollution. *Biol. J. Linn. Soc.* 29: 139-144.
- Newell, A.J., D.W. Johnson, and L.K. Allen. 1987. Niagara River biota contamination project-fish flesh criteria for piscivorous wildlife: New York State Department of Environmental Conservation, Division of Fish and Wildlife, Bureau of Environmental Protection, Technical Report 87-3.
- Nimmo, D.R. and C.J. Castle. 1998. A possible relationship between macroinvertebrate community structure and tissue-metals below mill tailings, Soda Butte Creek, Montana. Poster presentation, 19th Annual Meeting SETAC 15-19 November, Charlotte, NC.
- Oladimeji, A.A. and B.O. Offem. 1989. Toxicity of lead to *Clarias lazera*, *Oreochromis niloticus*, *Chironomus tentans* and *Benacus* sp. *Water Air Soil Pollut.* 44(3):191-201
- Pascoe, G.A., R.J. Blanchet, G.L. Linder, D. Palawski, W.C. Brumbaugh, T.J. Canfield, N.E. Kemble, C.C. Ingersoll, A. Farag, And J.A. DalSoglio. 1994. Characterization of ecological risks at the Milltown reservoir-Clark Fork river sediments superfund site, Montana. *Environ. Toxicol. Chem.* 13(12): 2043-2058
- Payst, B.M. 1994. Nesting ecology of the Osprey in the Spokane River corridor and implications for management. Washington State University. Written communication to C. Nuechterlein. June.
- Pelletier, G.J. 1994. Cadmium, Copper, Mercury, Lead, and Zinc in the Spokane River: Comparisons with water quality standards and recommendations for total maximum daily loads. Washington Department of Ecology, Environmental Investigations and Laboratory Services Program. Olympia, Washington. Pub. No. 94-99
- Pfieffer, D.E. 1985. A general assessment of the aquatic resources on the lower Spokane River reservoirs. Washington Water Power Company. September.
- Phipps, G.L., V.R. Mattson, and G.T. Ankley. 1995. Relative sensitivity of three freshwater benthic macroinvertebrates to ten contaminants. *Arch. Environ. Contam. Toxicol.* 28(3):281-286

- Plafkin, J.L., M.T. Barbour, K.D. Porter, S.K. Gross, and R.M. Hughes. 1989. Rapid bioassessment protocols for use in streams and rivers: benthic macroinvertebrates and fish. U.S. EPA Assessment and Watershed Protection Division, Washington D.C.
- Poels, C.L.M., M.A. van Der Gaag, and J.F.J. van de Kerkhoff. 1980. *Water Research*, 14:1029-1033
- Raucher, R.S., D. Peterson, Jr., R.E. Davis, and A. Michelsen 1990. Natural Resource Damages Associated with the Bunker Hill Superfund Site: Phase I: Limited Preassessment Screen. *Final Draft Report*. RCG/Hagler, Bailly, Inc. March
- Rehwoldt, R., L. Lasko, C. Shaw, and E. Wirhowski. 1973. The acute toxicity of some heavy metal ions toward benthic organisms. *Bull. Environ. Contam. Toxicol.* 10(5):291-294
- Reid, S.D. and O.G. McDonald. 1988. Effects of cadmium, copper, and low pH on ion fluxes in the Rainbow trout, *Salmo gairdneri*. *Can. J Fish. Aquat. Sci.* 45:244-253.
- Ridolfi Engineers. 1995. Surface water quality data compilation and evaluation for the Coeur d' Alene Basin Natural Resource Damage Assessment. August
- Roland, J. (unpublished) Plots of aqueous metals concentration in the Spokane River during 1998-9. Based on USGS data.
- Roark, S and K. Brown. 1996. Effects of metal contamination from mine tailings on allozyme distributions of populations of great plains fishes. *Environ. Toxicol. Chem.* 15(6): 921-927
- Saltes, J.G. and G.C Bailey. 1984. Use of fish gill and liver tissue to monitor zinc pollution. *Bull. Environ. Contam. Toxicol.* 32:233-237.
- Sauer, G.R. and N. Watabe. 1984. Zinc uptake and its effect on calcification in the scales of the mummichog, *Fundulus heteroclitus*. *Aquat. Toxicol.* 5:51-66.
- Sauer, G.R. and N. Watabe. 1989. Temporal and metal-specific patterns in the accumulation of heavy metals by the scales of *Fundulus heteroclitus*. *Aquat. Toxicol.* 14:233-248.
- Seitz, H.R., and M.L. Jones. 1981. Flow characteristics and water-quality conditions in the Spokane River, Coeur d'Alene Lake to Post Falls Dam, Northern Idaho. USGS. Open-file Report 82-102. October.
- Shearer, K.D. 1984. Changes in elemental composition of hatchery-reared Rainbow trout, *Salmo gairdneri*, associated with growth and reproduction. *Can.J. Fish. Aquat. Sci.* 41:1592-1600.
- Soltero, R.A., D.G. Nichols, and J.M. Mires. 1981. The effect of continuous advanced wastewater treatment by the City of Spokane on the trophic status of Long Lake, WA During 1980. WDOE 81-16. July.
- Soltero, R.A., D.M. Kruger, A.F. Gasperino, J.P. Griffin, S.R. Thomas, and P.H. Williams. 1976. Continued investigation of eutrophication in Long Lake, Washington: verification data for the Long Lake model. WDOE. 76-8. June.
- Spehar, R.L. and J.T. Fiandt. 1986. Acute and chronic effects of water quality criteria-based metal mixtures on three aquatic species. *Environ. Toxicol. Chem.* 5:797-806
- Stephan, C.E., D.I. Mount, D.J. Hansen, J.H. Gentile, G.A. Chapman, and W.A. Brungs. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. PB85-227049. National Technical Information Service, Springfield, VA.

- Stude, C.T. 1971. An analysis of water quality in the Spokane River. UW. Masters thesis.
- Suedel, B.C., J.H. Rodgers, Jr., and E. Deaver. 1997. Experimental factors that may affect toxicity of cadmium to freshwater organisms. *Arch. Environ. Contam. Toxicol.* 33(2):188-193
- Suter, G. W., II, A. E. Rosen, E. Linder, and D. F. Parkhurst. 1987. End points for responses of fish to chronic toxic exposures. *Environ. Toxicol. Chem.* 6:793–809.
- Suter, G. W., II, M. A. Futrell, G. A. Kerchner. 1992. Toxicological benchmarks for screening of potential contaminants of concern for effects on aquatic biota on the Oak Ridge Reservation, Oak Ridge, Tennessee. ORNL/ER-139. Oak Ridge National Laboratory.
- Suter, G. W., II. 1992. *Ecological Risk Assessment*. Lewis Publishers, Chelsea, MI.
- Suter G.W. and C.L. Tsao. 1996. Toxicological benchmarks for screening potential contaminants of concern for effects on aquatic biota. U.S. Department of Energy, ES/ER/TM-96/R2.
- Thomas, S.R. and Soltero, R.A. 1977. Recent Sedimentary History of a Eutrophic Reservoir: Long Lake, Washington. *J. Fish. Res. Board Can.* Vol.34.
- U.S. Environmental Protection Agency. 1980. Ambient water quality criteria for arsenic. EPA-440/5-80-021. Washington, DC.
- U.S. Environmental Protection Agency. 1980. Ambient water quality criteria for cadmium. EPA-440/5-80-025
- U.S. Environmental Protection Agency. 1980. Ambient water quality criteria for lead. EPA-440/5-80-057. Washington, DC.
- U.S. Environmental Protection Agency. 1980. Ambient water quality criteria for zinc. EPA-440/5-80-089. Washington DC
- U.S. Environmental Protection Agency. 1993. Water quality guidance for the Great Lakes System and correction; Proposed rules . Federal Register. 58(72):20802-21047.
- U.S. Environmental Protection Agency. 1995. Equilibrium partitioning approach to predicting metal bioavailability in sediments and the derivation of sediment quality criteria for metals. Volume I. EPA-822-D-94-002. Briefing Report to the EPA Science Advisory Board. Office of Water, Washington, DC.
- U.S. Environmental Protection Agency. STORET System.
- USGS Hydrologic Unit. 1997. Draft South Fork Coeur d'Alene watershed water quality subbasin assessment and draft TMDL. USGS. June
- USGS. 2000. *Water resources of Idaho*. URL: <http://idaho.usgs.gov/projects/spokane/download.html>. Accessed June 29, 2000.
- Varanasi, U. and D. Markey. 1978. Uptake and release of lead and cadmium in skin and mucus of coho salmon (*Oncorhynchus kisutch*). *Comp. Biochem. Physiol.* C60:187-191.
- Walker, C.H., S.P. Hopkin, R.M. Sibly, and D.B. Peakall. 1996. Evolution of Resistance to Pollution, Chapter 13, in *Principles of Ecotoxicology*, ed. G.M. Rand. Taylor & Francis. London, U.K.
- Wallace, J.B. and J.R. Webster. 1996 The role of macroinvertebrates in stream ecosystem function. *Annu. Rev. Entomol.* 41:115-139.
- WDOE.1995.1993-94 Investigation of PCBs in the Spokane River. Pub 95-310. February.

WDOE.1996. River and stream ambient monitoring data 1970-1996.

WDOE.1997. Spokane River - water quality results. WDOE. February.

Wills, E.D. 1985. The role of dietary components in oxidative stress in tissue. In H. Sies, ed., *Oxidative Stress in Tissues*. Academic Press, New York, NY.

Yake, W. 1979. Water quality trend analysis: the Spokane River Basin. WDOE.

Yake, W.E. 1977. Heavy metals in aquatic ecosystems: with special reference to the fish of the Spokane River, Washington. WSU.

Zheng, Y. 1995. Distribution of major and trace metals in groundwater of the Spokane Aquifer, Northeastern Washington: Water Quality and River/Aquifer Interaction. EWU. Master's thesis.